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TABLE OF CONTENTS

Vol. 28 February 1, 1945 No. 2

Journal of The American Ceramic Society

Factors Influencing Fluxing Action of Various Oxides in Low-Temperature Borosilicate Glasses. . 33–36
By Howard R. Swift

Standard Thermal-Shock Test for Porcelain Enameled Utensils 36–41
By F. A. Petersen and A. I. Andrews

Effect of Temperature on Homogenizing Rate of Soda-Lime-Silica Glass 42–47
By R. L. Tiede and F. V. Tooley

Raw Leadless Whiteware Glazes 48–52
By C. G. Harman and H. R. Swift

Study of Glaze Penetration and Its Effect on Glaze Fit: Parts I–III 52–62
By Everett Thomas, M. A. Tuttle, and Esther M. Miller

Use of Potassium Dichromate Method in Determining Iron Content of Pickle Acids 62–64
By Edward G. Porst

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Vol. 28 February 1, 1945 No. 2

FACTORS INFLUENCING FLUXING ACTION OF VARIOUS OXIDES IN LOW-TEMPERATURE BOROSILICATE GLASSES*

By Howard R. Swift

Abstract

Strontium, barium, and lead oxides were studied as fluxes in low-temperature borosilicate glasses by using the button-flow method. It was found that strontia may be superior to lead oxide as a flux in glasses high in fluorides and low in alumina. This result was explained by the greater solubility of fluorides in strontia glasses, in which case the two fluxes, strontia and fluorspar, are acting together.

I. Introduction

The use of strontium compounds in enamel compositions has been rather limited for two reasons, (1) the relative scarcity of strontium compounds and (2) the intermediate position of strontium between calcium and barium, which suggests that any improvement that can be secured with strontium could probably be duplicated with an addition of a mixture of calcium and barium. Since the wartime production of strontium compounds has increased to such a point that this material is readily available, an investigation was undertaken to determine any specific advantages which might be gained by the use of strontium in enamel compositions.

Because strontium is one of the alkaline earths, it should play the role of a flux in enamel glasses. This investigation was concerned with the fluxing ability of strontium oxide as compared with other oxide fluxes commonly used in enamel compositions.

II. Replacement of Fluxes in Enamels with Strontia

(1) Field of Study

In the preliminary study of the fluxing action of strontium oxide in enamels, five types of enamels were studied. The compositions, shown in Table I, include (A) a sheet-steel ground-coat,[1] in which additions of strontium and barium carbonate were compared; (B) a clear, wet-process, cast-iron, cover-coat enamel[2] designed for use with colors, in which strontia replaced the barium, calcium, and zinc oxides; (C) a white, wet-process, cast-iron, cover-coat enamel,[3] in which strontia replaced the lead, zinc, barium, and calcium oxides; (D) a dry-process, cast-iron, cover-coat enamel,[3] in which strontia replaced the calcium, barium, zinc, and lead oxides; and (E) a sheet-steel, cover-coat enamel, in which the fluorides of calcium, lithium, and strontium were compared.

Table I

Enamel Compositions Used in Preliminary Study of Some Relations Between Composition and Fusibility

	Composition (%)				
	A	B	C	D	E
KNaO	19.9	11.0	11.6	12.7	17.0
B_2O_3	13.8	24.7	12.2	8.1	8.9
Al_2O_3	6.9		4.6	8.2	5.4
SiO_2	49.4	27.0	24.5	24.3	49.0
CaO	5.0	12.8	5.6	3.7	2.6
F_2	3.4	5.8	5.0	4.1	1.8
CoO	0.6				
MnO_2	1.9				
BaO		16.0	8.2	3.1	5.7
ZnO		5.0	8.0	10.4	
PbO			17.6	16.6	
Sb_2O_3			3.9		9.7
SnO_2				9.0	
Total	100.9	102.3	101.2	100.2	100.1

(2) Procedure

Enamel batches of 2000 gm. each were smelted in laboratory crucible smelters. The fusibilities of the resulting glasses were compared by using the button-flow method.[4] Cylindrical specimens of $2^1/_2$ gm. each

* Preprinted for the Forty-Seventh Annual Meeting, The American Ceramic Society, Buffalo, N. Y., April 15–19, 1945 (Enamel Division). Received October 2, 1944.

[1] A. I. Andrews, Enamels, p. 170. Twin City Publ. Co., Champaign, Ill., 1935. 428 pp.; Enamel Bibliography, 1944 ed., p. 12.

[2] B. Niklewski, Jr., and A. I. Andrews, "Wet-Process Leadless Cast-Iron Enamels," *Jour. Amer. Ceram. Soc.*, **23** [6] 178–85 (1940).

[3] A. I. Andrews and R. L. Cook, Enamel Laboratory Manual. Garrard Press, Champaign, Ill., 1941. 64 pp.; *Ceram. Abs.*, **21** [1] 7 (1942).

[4] C. J. Kinzie, "Method for Study of Relative Viscosity of Enamel Glasses," *Jour. Amer. Ceram. Soc.*, **15** [6] 357–60 (1932).

TABLE II

THEORETICAL COMPOSITIONS OF GLASSES STUDIED TO DETERMINE CHARACTERISTICS OF COMPOSITIONS IN WHICH STRONTIA EXERTS MAXIMUM FLUXING ACTION

Series	Base	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
Na_2O	11.0	11.0	11.0	11.0	11.0	11.0	11.0	11.0	11.0	11.0	11.0	11.0	11.0	11.0	11.0	11.0	11.0
SiO_2	27.0	35.0	27.0	27.0	27.0	27.0	27.0	27.0	27.0	27.0	27.0	27.0	35.0	35.0	35.0	35.0	35.0
B_2O_3	24.7	24.7	18.0	10.0	24.7	24.7	24.7	24.7	24.7	24.7	24.7	24.7	16.7	16.7	16.7	16.7	16.7
Al_2O_3					5.0	10.0											
CaF_2	11.9	11.9	11.9	11.9	11.9	11.9	6.0		11.9	11.9	11.9	11.9	11.9	11.9	11.9	11.9	11.9
CaO	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2		4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2
ZnO	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0		5.0	5.0					
Na_3AlF_6											10.0						
Sb_2O_3												5.0	5.0	5.0	5.0	5.0	5.0
SrO, BaO, or PbO	16.2	16.2	16.2	16.2	16.2	16.2	16.2	16.2	16.2	16.2	16.2	16.2		4.0	8.0	12.0	16.2

were prepared from frit which was ground to pass a No. 80 screen and was retained on a No. 200 screen. The specimens were placed in a row on a 4- by 4-in. ground-coated, steel panel. The panel was placed in a furnace in a horizontal position and was heated for three minutes, after which the panel was lowered to a vertical position. The buttons were allowed to flow until the longest one was approximately 7 cm. long, after which the panel was removed from the furnace. The type of enamel governed the temperature at which the buttons were allowed to flow.

(3) Results

It was found that strontia behaved very differently as a flux depending on the type of enamel in which it was placed. In enamel A, strontia and baria had similar fluxing properties; in enamel B, the glass containing strontia flowed more than any of the other glasses in the series, including a similar one containing lead oxide; in enamel C, strontia was slightly inferior to lead, barium, and zinc oxides as a flux; in enamel D, strontia was very inferior to lead, barium, and zinc oxides as a flux; and in enamel E, the fluoride of strontium was comparable to fluorspar and inferior to lithium fluoride as far as the fluxing ability was concerned.

III. Effect of Composition Changes on Fluxing Ability of Strontium, Barium, and Lead Oxides

(1) Discussion

It was the purpose of this phase of the investigation to determine which characteristics of composition are responsible for the activity of strontia as a flux in some instances and its relatively poor fluxing ability in other cases. A series of glasses was also made to determine whether strontia, baria, and lead oxide have the same relative fluxing ability when introduced in smaller quantities.

(2) Field of Study

The theoretical compositions of the glasses studied are shown in Table II. The base glass has the same composition as enamel B (section II), in which strontia was very active as a flux. In series A to K, variations were made in the base composition, one component at a time, and the effect on the relative fluxing actions of strontia, baria, and lead oxides was noted. In series L to P, the base composition was held constant and the amounts of strontia, baria, and lead oxide were varied.

(3) Procedure

Batches of 100 gm. of each glass were prepared, screened, mixed, smelted at 1900°F. in an electric smelter, and quenched in water. The fusibilities were compared by using the button-flow method as previously described. Each set of buttons was allowed to flow until the longest one of the set was about 7 to 8 cm. long; consequently, comparisons can be made only between strontium, barium, and lead glasses in each set. This was necessitated by the increased refractoriness of some of the series with changes in the composition. All of the buttons in series L, M, N, O, and P were run at the same time and temperature.

(4) Results

The lengths of flow of the glasses of series A to K are shown in Fig. 1. With the base composition, the strontia glass was more fusible than the lead glass, while the barium glass was intermediate in fusibility. Essentially the same order of fusibility prevailed when the boric oxide was decreased (series B and C), when the fluorspar was slightly decreased (series F), when the lime was omitted (series H), when cryolite was added (series J), or when antimony oxide was added (series K). The lead oxide glasses were slightly more fusible than the corresponding strontia glasses when the silica was increased (series A), when the alumina was increased 5% (series D), or when the zinc oxide was omitted (series I). There was a sharp reversal in the order of fusibility when 10% of alumina was added to the base composition (series E) or when fluorspar was omitted from the base composition (series G).

Figure 2 shows that with a variable amount of strontium, barium, and lead oxides added to a borosilicate glass, the same order of fusibilities prevailed regardless of the amount of flux added. The strontia glass was more fusible than the barium glass, which was more fusible than the lead glass with any given percentage of flux added.

IV. Effect of Fluorspar and Alumina on Fluxing Ability of Strontium, Barium, and Lead Oxides

(1) Discussion

Strontia has been shown to exert its greatest fluxing action, relative to lead and barium oxides, in glasses high in fluorspar and low in alumina. There were differences in the opacity of the button-flow specimens caused apparently by variations in fluoride solubility in the various glasses. In this phase of the investiga-

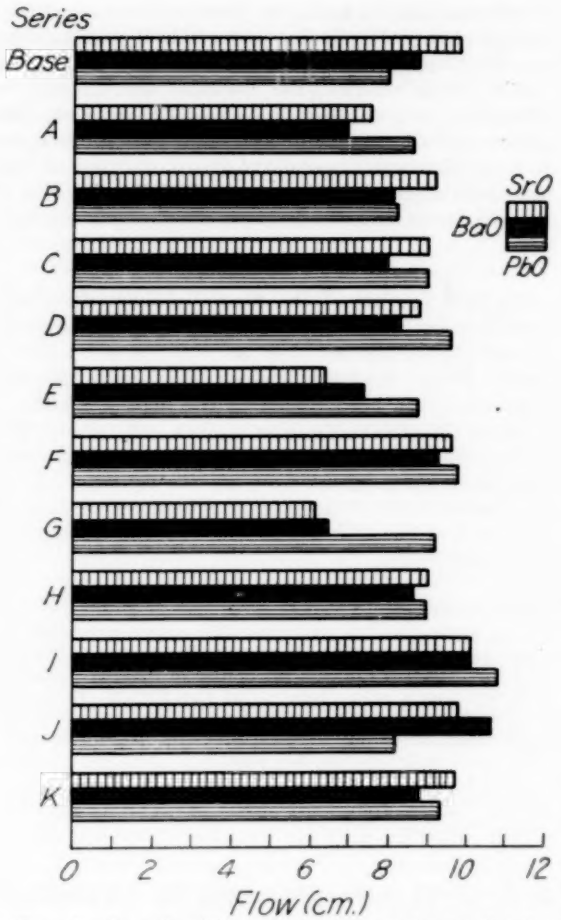

FIG. 1.—Length of flow of button specimens showing some relation between composition and fusibility for low-temperature borosilicate glasses.

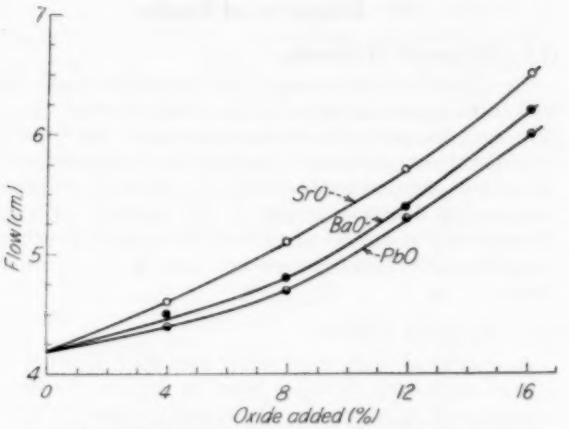

FIG. 2.—Effect of varying the amount of strontium, barium, and lead oxides on fusibility of a borosilicate glass (series L, M, N, O, and P, see Table II).

TABLE III

THEORETICAL COMPOSITIONS OF GLASSES STUDIED TO DETERMINE EFFECTS OF VARYING ALUMINA AND FLUORSPAR ON RELATIVE FLUXING ACTION OF STRONTIUM, BARIUM, AND LEAD OXIDES

	Composition					
Series	A	B	C	D	E	F
Silica	42	42	42	42	42	42
Sodium oxide	13	13	13	13	13	13
Calcium oxide	5	5	5	5	5	5
Boric oxide	20	20	20	20	20	20
Aluminum oxide				10	10	10
Strontium oxide	20			20		
Barium oxide		20			20	
Lead oxide			20			20
Fluorspar	Variable					

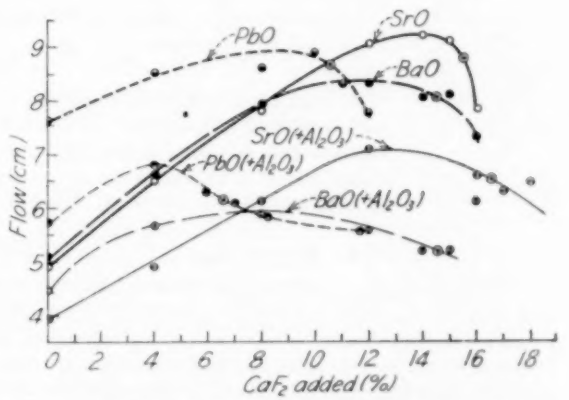

FIG. 3.—Effect of CaF_2 on fusibility of borosilicate glasses containing SrO, BaO, and PbO.

tion, fluoride solubility was determined in glasses varying in alumina content and containing strontia, baria, or lead oxide.

(2) Procedure

The theoretical compositions of the glasses studied are shown in Table III. The glasses were smelted at 1900°F., cooled in the furnace to 1500°F., held there for three hours to allow fluoride crystallization to take place, removed from the furnace, and air cooled. The fluoride solubility was determined by visual examination. The relative fusibilities were obtained by using the button-flow method as before. All buttons were allowed to flow vertically at 1500°F. for eight minutes.

(3) Results

The lengths of flow of the resulting glasses as a function of the fluorspar content are shown in Fig. 3. The solubility limit, as obtained by visual examination, is indicated on each curve as a circle and center dot. With a low fluorspar content, the lead glass was more fusible than the barium glass, which was more fusible than the strontia glass With a higher fluorspar content, the order was reversed. All of the glasses decreased in fusibility with increasing fluorspar after a point approximately at the solubility limit was reached. More fluoride was soluble in the strontia glass than in the lead glass, while the barium glass was intermediate in fluoride solubility. Additions of alumina caused a decrease in the amount of fluorspar required for maximum fusibility for all glasses.

V. Discussion of Results

(1) Statement of Results

Strontia acts as a stronger flux than either baria or lead oxide in certain types of glass compositions. Low silica and the presence of zinc oxide assist the fluxing action of strontia relative to the lead to a certain degree, but a low alumina content and the presence of large amounts of fluorspar appear to be essential. Fluoride solubility is greatest in glasses containing strontia, intermediate in baria glasses, and lowest in lead oxide glasses.

(2) Analysis of Data

It is evident that the greater fusibility of strontia glasses containing fluorspar must be due to the high solubility of fluorides in the strontia glasses. Both fluxes act together to give very fusible glasses. On the other hand, in glasses containing lead oxide, the fluoride is less soluble and the crystallized fluoride gives no fluxing action. The combined fluxing action of lead oxide plus a small quantity of fluorspar is less than the action of strontia plus a greater quantity of fluorspar in solution. The strontia glass is therefore more fusible. The glasses containing barium oxide are intermediate in fluoride solubility and in fusibility.

The role of alumina is not quite as evident as that of fluorspar in affecting the relative fusibilities of these glasses. The increased viscosity caused by the addition of alumina tends to keep the fluorides from crystallizing if the glasses are quenched from the smelting temperature as was done in section III. Both lead and strontium glasses have a large quantity of fluorspar in solution, and the lead glass shows a greater fusibility owing to the greater fluxing power of lead oxide as compared with strontia alone. If the glasses, however, are cooled slowly so that the fluorides are allowed to crystallize, as was done in section IV, more fluoride goes out of solution in the lead oxide glass than in the strontia glass, even though the alumina is present, and the strontia glass has the greater fusibility because of this greater quantity of fluorspar remaining in solution.

VI. Summary

An investigation of the fluxing ability of strontia relative to baria and lead oxide in low-temperature borosilicate glasses has revealed that strontia is a superior flux in glasses high in fluorspar and low in alumina. This effect has been traced to the high solubility of fluorides in strontia-bearing glasses. A substitution of strontia for lead oxide in low-temperature borosilicate glasses may either decrease the fusibility, if the fluorspar is low and the alumina is high, or increase the fusibility, if the alumina is low and the fluorspar is moderately high.

Acknowledgment

The author wishes to express his appreciation for the assistance and encouragement offered by C. G. Harman and A. I. Andrews during the course of this investigation. Appreciation is also extended to the Barium Reduction Corporation of South Charleston, W. Va., sponsors of a cooperative fellowship at the University of Illinois under which this investigation was made.

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STANDARD THERMAL-SHOCK TEST FOR PORCELAIN ENAMELED UTENSILS*

By F. A. Petersen and A. I. Andrews

Abstract

The equipment and method used in testing porcelain enameled utensils for thermal-shock resistance is described. Test results are given which show that increased enamel thickness and decreased metal thickness decrease the thermal-shock resistance of enameled ware. The mechanics of thermal-shock failures is discussed. This study is one of a series sponsored by the Enameled Utensil Manufacturers' Council.

I. Introduction

Since enameled utensils which are used for kitchen and hospital ware are subjected to sudden temperature changes, it is desirable to have a test for resistance to thermal shock and to obtain thereby further information concerning the various factors such as the enamel composition, design, and processing which influence this property. It was the object of the present work to develop a reliable and convenient test and to evaluate some of these factors.

II. Review of the Literature

Various tests have been used to determine the thermal-shock resistance of enamels applied to steel. Shaw,[1] Landrum,[2] and Danielson and Sweely[3] heated the enameled specimens, then plunged them into cold water and noted the effects. The procedures varied in respect to the temperature to which the specimens were heated and the manner in which they were heated. Robson[4] heated enameled pieces in a muffle and then quenched them in water, increasing the temperature of heating each cycle until failure occurred.

* Presented at the Forty-Sixth Annual Meeting, The American Ceramic Society, Pittsburgh, Pa., April 4, 1944 (Enamel Division). Received August 21, 1944.

[1] J. B. Shaw, "Testing Sheet-Steel Enamels," *Trans. Amer. Ceram. Soc.*, **12**, 463–93 (1910).

[2] R. D. Landrum, "Comparison of Ten White Enamels," *ibid.*, **14**, 489–509 (1912).

[3] R. R. Danielson and B. T. Sweely, "Relations Between Composition and Properties of Enamels for Sheet Steel," *Jour. Amer. Ceram. Soc.*, **6** [10] 1011–29 (1923).

[4] J. T. Robson, "Comparative Crazing and Chipping of Wet- and Dry-Process Cast-Iron Enamels, *ibid.*, **7** [7] 563–66 (1924).

Wolfram and Harrison[5] heated enameled plates containing 25 cc. of water over a Bunsen burner until the water was evaporated, then heated the plate dry for 15 seconds, after which 25 cc. of water were added to the plate, and the procedure was repeated until the plate failed or ten cycles had been completed. This is the first recorded test where the entire piece was not quenched by plunging into water and also the first test where an attempt was made to simulate the condition under which the ware was used.

Kinzie[6] developed a test in which the enamel to be tested was applied to a steel plate and the plate was heated, from below, to a temperature of 680°F. Water was then allowed to drop onto the plate at the rate of three drops per minute for one-half hour. The plate was then inspected for any crazing or chipping and the enamel was rated according to the appearance of the tested area. Shands[7] devised a test similar to that used by Kinzie. Another method for testing thermal-shock and crazing resistance, devised by Kinzie,[8] involved the use of an electrically heated oven which had a very accurate temperature control. The test sample was a 6- by 4-in. steel plate coated with the enamel to be tested. The specimen was heated in the oven to a specified temperature for a set length of time and then removed and quenched with water. The temperature of the quenching water was carefully controlled. Other writers[9] have described tests which consist of placing an enameled pan containing a set amount of water on a hot plate and either bringing it to a boil or taking it to dryness, after which a similar amount of water is added and the test repeated. The rating depended on the number of cycles which the pan passed without chipping. Bryant[10] described a method used for testing porcelain enameled cooker inserts which consisted of heating the cooker-insert bottom until it attained a temperature of 500°F. It was then quenched by adding enough water to cover the bottom of the specimen; this water was evaporated by continued heating, and, when the bottom again attained a temperature of 500°F., the procedure was repeated. The test was repeated five times or until the enamel failed. Howe and Bolin[11] used an electric roaster for the heating unit and the enameled pan to be tested was placed in the roaster which was set at 350°F. The specimen was heated for $^1/_2$ hour and then 50 cc. of ice water were added to it; after $^1/_2$ hour, the procedure was repeated. The pan was quenched three times and if no failure occurred the temperature was increased 50°; three cycles were completed at this temperature and if no failure occurred the temperature was increased another 50°. This procedure was repeated until 500°F. was reached or the pan failed. The enameled pan was rated according to the number of cycles passed before chipping occurred.

In many investigations of the effect of the general properties of enamelware on its thermal-shock resistance, it was found by all investigators[12] that a thin enamel coating was more resistant to thermal shock than a thick one.

Several investigators studied the effect of the coefficient of expansion of the enamel on thermal-shock resistance. Sweely,[12(c)] Danielson and Sweely,[3] Hansen,[9(c)] McIntyre,[9(d)] Shands,[7(b)] and Howe and Bolin[11] found that a combination of a high-expansion, ground-coat enamel and low-expansion, cover-coat enamel gave the best resistance to thermal-shock failure. Sasse[12(e)] stated that it is best to have a low-expansion ground coat but that it should be under 320×10^{-7} (which is high) and a low-expansion cover coat, not over 300×10^{-7}. Harrison and Wolfram[5(b)] say that the coefficient of expansion of a ground coat, when no cover coat is applied to it, does not seem to be a controlling factor as far as thermal-shock resistance is concerned. Vielhaber[12(d)] states that the expansion of the enamel should follow the expansion of the iron and that only one coat of enamel should be applied to the inside of

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[5] (*a*) H. G. Wolfram and W. N. Harrison, "Effect of Composition on Properties of Sheet-Steel Enamels," *Jour. Amer. Ceram. Soc.*, **8** [11] 735–55 (1925).

(*b*) W. N. Harrison and H. G. Wolfram, "Effects of Composition on Properties of Ground-Coat Enamels for Sheet Steel," *ibid.*, **10** [3] 163–79 (1927).

[6] C. J. Kinzie, "Physical Tests for Vitreous Enamels, I," *ibid.*, **12** [3] 188–92 (1929).

[7] E. H. Shands, "Thermal-Shock Test for Porcelain Enamel, I–II," *Amer. Enameler*, (*a*) **5** [2] 8–9; (*b*) [3] 11 (1932); Enamel Bibliography, 1944 ed., p. 247.

[8] C. J. Kinzie, "Apparatus for Testing Enamels and Glazes for Resistance to Crazing Under Thermal Shock," *Jour. Amer. Ceram. Soc.*, **15** [2] 112–15 (1932).

[9] (*a*) M. G. Ammon, "Physical Testing Laboratory," *Enamelist*, **11** [12] 13–14 (1934); Enamel Bibliography, 1944 ed., p. 11.

(*b*) A. I. Andrews, Enamels, pp. 338–39. Twin City Publishing Co., Urbana, Ill., 1935; Enamel Bibliography, 1944 ed., p. 12.

(*c*) J. E. Hansen, Manual of Porcelain Enameling, pp. 240–44. Enamelist Publishing Co., 1937; Enamel Bibliography, 1944 ed., p. 112.

(*d*) G. H. McIntyre, "Physical Testing of Porcelain Enameled Hollow Ware," *Proc. Porcelain Enamel Inst. Forum, First Forum*, May, 1937, pp. 155–63; Enamel Bibliography, 1944 ed., p. 183.

(*e*) E. E. Bryant, "Standard for Porcelain Enameled Utensils," *Enamelist*, **17** [6] 33–34 (1940).

[10] E. E. Bryant, "Porcelain Enameled Cooker Inserts," *Enamelist*, **19** [6] 10–11 (1942); *Ceram. Abs.*, **21** [8] 165 (1942).

[11] E. E. Howe and E. P. Bolin, "Resistance of Enamels to Thermal Shock," *Jour. Amer. Ceram. Soc.*, **26** [Nov. 1, 15], 463–66 (1942).

[12] E. H. Shands, R. H. Turk, and H. G. Wolfram, "Factors Causing Variations of Results in Tests for Physical Properties of Enamels," *ibid.*, **15** [8] 438–43 (1932).

(*b*) "Thickness of Enamel Layers," *Émail* (in *Emailwaren-Ind.*, **7** [48]), **2** [11] 68–69 (1930); Enamel Bibliography, 1944 ed., p. 272.

(*c*) B. T. Sweely, "Relation of Composition to Thermal Shock in Steel Enamels," *Jour. Amer. Ceram. Soc.*, **5** [5] 263–65 (1922).

(*d*) L. Vielhaber, "Cracking of Cooking Utensils," *Emailwaren-Ind.*, **10** [40] 317–21 (1933); Enamel Bibliography, 1944 ed., p. 284.

(*e*) Heinrich Sasse, "Cracked Cooking Utensils," *Emailwaren-Ind.*, **11** [6] 47–50 (1934); Enamel Bibliography, 1944 ed., p. 239.

(*f*) R. Aldinger, "Causes and Prevention of Chipping of Enameled Cookingware," *Keram. Rundschau*, **42** [32] 394–95 (1934); *Ceram. Ind.*, **23** [3] 134, 136–37 (1934); listed as "Boiling Strength of Enameled Ware," in Enamel Bibliography, 1944 ed., p. 3.

See also references 7(*b*), 9(*c*), 9(*d*), and 11.

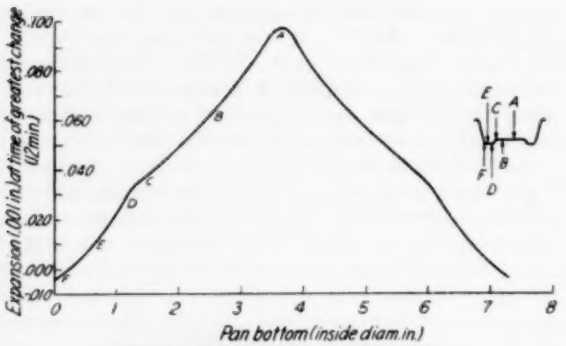

FIG. 1.—Expansion vs. diameter.

enameled pans. Other investigators[13] state that the expansion of the enamel should be low for good thermal-shock resistance.

It was mentioned by some writers* that thermal-shock resistance of enameled ware was increased with increased thickness of the base metal.

Vielhaber[12(d)] and Aldinger[12(f)] state that the shape of the bottom of the pan influences its thermal-shock resistance.

III. Preliminary Investigation

The development of a thermal-shock test is particularly difficult because of the many variables involved. On investigation of service failures, however, practically all of these failures were found to be associated with heating the ware on top of the stove or by abusive quenching of hot pans by pouring cold water into them. It was therefore decided to develop a test which would simulate this kind of treatment.

Zink,† in some early work on the problem, showed that the bottom of a pan during heating and cooling actually raises and recedes with the rise and fall of the temperature when it is heated over a hot surface. Using an Ames dial, he determined the amount of movement of the pan bottom; his results are shown in Fig. 1. These data led to the belief that so-called thermal-shock failures are actually stress failures caused by this movement of the pan bottom. The stresses set up during this heating and cooling of the pan bottom are, however, very complicated, and it was decided to use heat to develop these stresses in working out a test method.

After a comparison of various heat sources, such as gas hot plates, molten baths, and electric hot plates, a commercial type of electric hot plate was selected as being the most easily controlled, convenient, and suitable heat source for a test method.

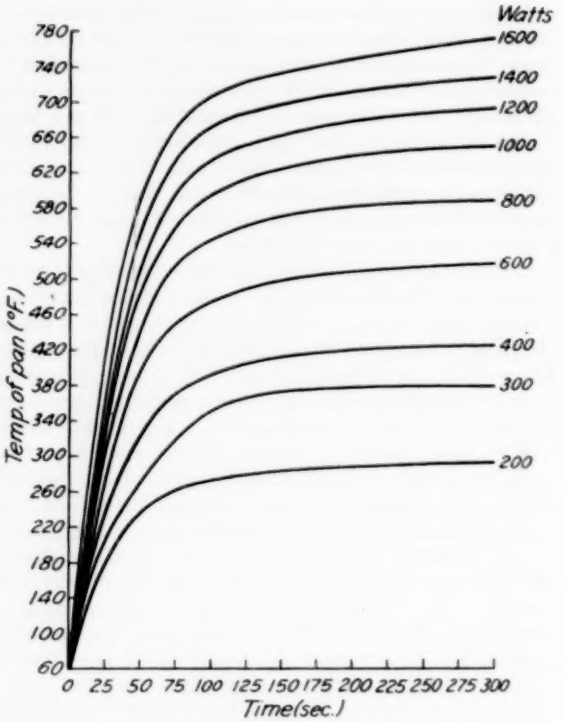

FIG. 2.—Heating rates of enameled pan at various hot-plate temperatures.

The general test procedure consisted of bringing to the boiling point a set amount of water in a test pan which rested on the electric hot plate; the water was then poured from the test pan, and the pan was dried and replaced on the hot plate, where it remained in place for a predetermined time; the same amount of water that was added at the start of the test was then poured into the pan and brought to a boil. This procedure was repeated until failure occurred or until ten cycles were completed. The pan was rated according to the number of cycles it passed successfully.

It was found, however, that the results obtained under these conditions did not always correlate with the results obtained in actual usage of the pans.

In an effort to establish the cause of these differences, the characteristic heating curves for pans at different hot-plate temperatures were determined (see Fig. 2). These data were obtained by welding a Chromel-Alumel thermocouple to the inside bottom of an enameled pan. The enamel was ground off down to the base metal at the spot where the couple was attached to the pan. The power input to the hot plate was then set at a given wattage, and the plate was allowed to heat long enough to reach equilibrium. The test pan was then placed on the plate and temperature readings were recorded as the heating of the pan progressed. From these data, it was noted that unless the dry-heating period was fairly long, at least two minutes, the pan was not up to temperature and that slight errors in timing would

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[13] (*a*) "Relation Between Enamel and Steel Studied by the U. S. Bureau of Standards," *Ceram. Ind.*, **6** [6] 586 (1926); *Ceram. Abs.*, **5** [11] 344 (1926).

(*b*) Ludwig Stuckert, "Expansion of Enamels," *Ceram. Age*, **17** [5] 269–72 (1931); Enamel Bibliography, 1944 ed., p. 265.

(*c*) L. D. Fetterolf, "Effect of Zinc Oxide on Sheet-Iron Cover-Enamel Properties," *Jour. Amer. Ceram. Soc.*, **16** [7] 319–24 (1933).

See also reference 12(*f*).

* See references 9(*c*), 9(*d*), and (*d*), (*e*), and (*f*) of reference 12.

† G. H. Zink, unpublished data.

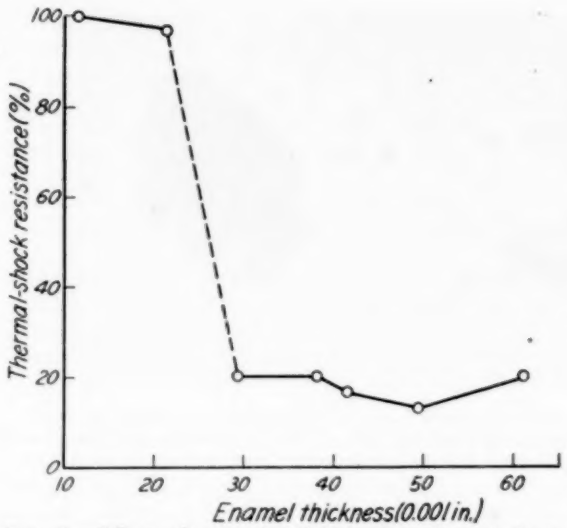

FIG. 3.—Effect of enamel thickness on thermal-shock resistance.

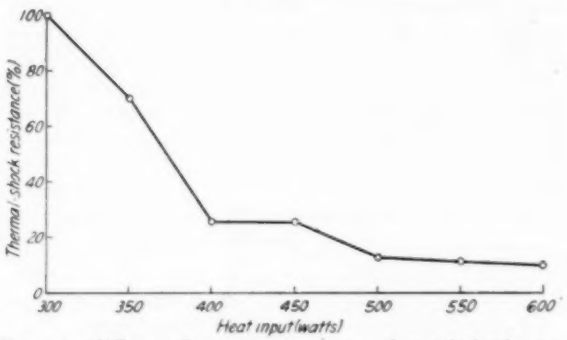

FIG. 4.—Effect of temperature on thermal-shock resistance.

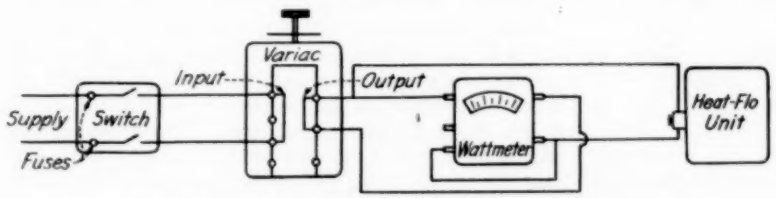

FIG. 5.—Wiring diagram for thermal-shock test.

cause a marked difference in the temperature of the pan bottom. Based on these results, the dry-heating period was set at three minutes so that all pans would actually be tested at the same temperatures.

Another step in the development of the test consisted of heating a dry pan for three minutes on a hot plate at a set temperature and then quenching with a set volume of water at a specified temperature. This procedure was repeated for ten cycles or until the pan failed. This test was used as a tentative standard and was capable of classifying one-, two-, and three-coat ware, and it also brought out any differences between the ware in each of the above groups. The effect of enamel thickness was studied using this test, and the results of this work are shown in Fig. 3.

As the industry improved the thermal-shock resistance of the ware, it was found necessary to change the test conditions so that they would be more severe. To accomplish this, a series of pans was tested with the hot plate set at different temperatures. The results of tests using this method are shown in Fig. 4. It is obvious that the severity of the test increased with each cycle.

On the basis of these test data and the experience and knowledge gained in the stepwise development, the standard thermal-shock test used by the members of the Enameled Utensil Manufacturers' Council was developed.

IV. Standard Test Procedure

(1) Apparatus

The equipment used for the standard thermal-shock test is the same as is used for the EUMC standard solubility test.[14] This equipment consists of (1) Heat-Flo SB-2000 115–120 volt, 2000-watt electric hot plate; (2) wattmeter, scale 0–3 kw., 75–150 volts, 20 cycles; (3) Variac, 100–Q or 100–R, transformer; and (4) a sweep-hand timer. The apparatus is wired as shown in Fig. 5.

(2) Preparation for Test

(1) Five pans, which comprise a test sample, should be brought to room temperature before being tested.

(2) Preheat the hot plate, with the high-heat switch on, at 300 watts heat input for at least one hour.

(3) Adjust the temperature of the quenching water to 70° ± 2°F.

(3) Test Procedure

(1) Place a dry test pan, at room temperature, on the center of the hot plate and allow it to remain in position for three minutes.

(2) Remove the pan from the hot plate and quench with enough water to fill the pan to a depth of 1 in.

(3) After ten (10) seconds, empty the pan and wipe the inside of the pan as dry as possible with a damp sponge.

(4) At the end of a total non-heating period of twenty (20) seconds, replace the pan on the center of the hot plate.

(5) Immediately increase the watt input to the hot plate 50 watts and heat the pan dry for 8 minutes; then repeat the above procedure.

(6) After reaching 600 watts, increase the watt input 100 watts each cycle until 1000 watts is reached.

(7) The test is terminated either when the enamel fails or 1000 watts is reached.

(8) Record the rating for the pan; this rating is one cycle below the cycle where the enamel failed.

(9) The results of tests on the five pans in the sample

[14] F. A. Petersen and A. I. Andrews, "Enameled Utensil Manufacturers' Council Tentative Standard Solubility Test for Porcelain Enameled Cooking Utensils," *Jour. Amer. Ceram. Soc.*, **27** [4] 113–15 (1944).

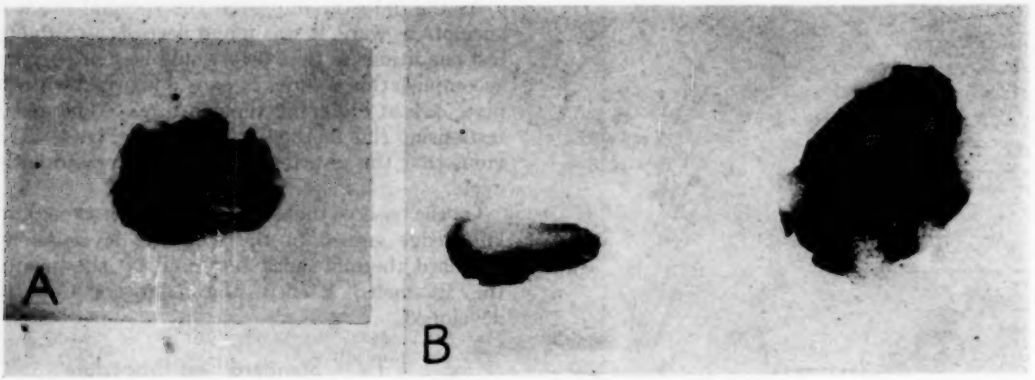

FIG. 6.—Typical thermal-shock failures; (*A*) failure over large area, enamel popped off on failure; (*B*) both types of failures on same pan; the spall has been removed from fracture on left. *Note:* An example of small-type failure is too small for reproduction; a small piece of enamel popped off, but the chip or spall remained intact.

Pan No.	Cycle of failure	Rating
1	6	5
2	5	4
3	6	5
4	5	4
5	4	3
		21

$$\frac{21}{5} = 4.2 \text{ cycles (rating of sample)}$$

are averaged to obtain the rating for the sample(p. 40).

Definition of Failure: A failure is the removal of enamel from the pan, generally accompanied by a cracking noise. Fish-scaling and crazing are not considered failures unless enamel is removed from the pan bottom.

TEST SCHEDULE

Cycle	Watt input	Cycle	Watt input
1	300	7	600
2	350	9	700
3	400	11	800
4	450	13	900
5	500	15	1000
6	550		

V. Tests

A series of standard shaped two-quart pudding pans was submitted for test by an enamelware manufacturer. Pans were prepared in eleven different metal thicknesses and were finished in one-coat mottled gray, in two-coat white, and three-coat white enamel. The pans were tested using the standard procedure.

The enamel thickness was determined with a G. E. magnetic thickness gage[15] at four or more points on the inside and outside bottom of the pan. These values were averaged and that value was taken as the enamel thickness on the pan.

The metal thickness was determined on sections which were cut from the bottom of at least eight pans of each metal thickness. These sections were de-enameled in molten caustic and the metal thickness was measured, using a micrometer caliper, and averaged.

[15] "New G. E. Thickness Gage for Curved and Plane Surfaces," *Better Enameling*, **10** [1] 28 (1939).

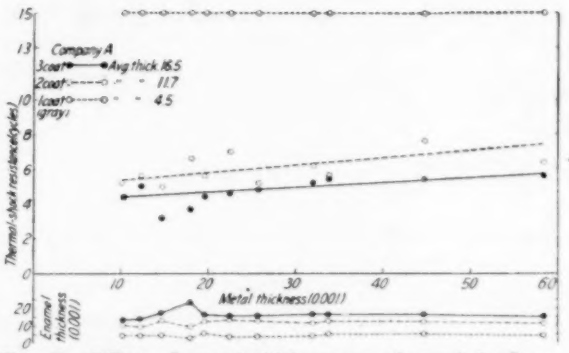
Company A
1 coat Avg thick 18.5
2 coat " " 11.7
1 coat (gray) " " 4.5
Thermal shock resistance (cycles)
Metal thickness (0.001)
Enamel thickness (0.001)

FIG. 7.—Effect of metal thickness on thermal-shock resistance: one-, two-, and three-coat ware.

VI. Discussion of Results

Figure 1 shows that during heating, the expansion of the pan bottom causes a decided "crowning." Since the edges of the bottom are held firmly in position, the greatest stress is set up close to the edge and the upward movement of the bottom is restrained at this point. It is in this region, close to the outer edge of the bottom, that thermal-shock failures most frequently occur. The authors believe that it is this so-called "breathing" of the pan bottom during heating and rapid cooling which causes thermal-shock failures. Irregularities in the bottom of a pan are also a source of failure during thermal-shock testing. A cover-coat enamel with a low coefficient of expansion is reported by all who have worked on this problem as being necessary for the best thermal-shock resistance. With this condition, the compression within the cover-coat layer is increased owing to the difference in the coefficients of expansion of the enamel and the base metal. As the pan bottom is deflected upward, the degree of possible deflection is increased with increased compression in the enamel layer because the tensile stress under which the enamel layer is placed by the upward deflection is not applied until the enamel layer changes from compression to tension. This change takes place as the deflection of the enamel layer is increased. The

enamel fails after the compression has been overcome within the layer and the tensile stress is applied directly to the enamel layer.

The failure of the enamel usually occurs during the heating of the pan and very rarely during quenching. An indiscernible crazing of the top surface of the cover coat may take place on quenching, but it is the deflection of the pan bottom which causes the troublesome complete fracture and the removal of the enamel. This explanation can also account for the deleterious effect of a thick enamel coating since it is known that such coatings cannot withstand as great a deflection before failure as can a thin enamel coating.

A careful examination of failures caused by thermal shock indicates that these failures are similar to those caused by mechanical deflection. Figure 6 shows two typical types of thermal-shock failures, (1) a type where the enamel spalls but is not completely removed from the surface and (2) a type where the enamel actually separates in a large area. There seems to be no correlation between the types of failure caused by thermal shock and the thickness of enamel, the kind of enamel, or the processing. Figure 6 (*B*) shows two fractured areas resulting from thermal shock on the same pan; the one on the left is a spall from which the chip was mechanically removed with a knife blade and that on the right resulted from spontaneous chipping during the test. The ridges which appear in the ground-coat enamel under these chips are an indication that the enamel was broken in tension and are characteristic of mechanical deflection failures.

Figure 7 shows that thermal-shock resistance increases slightly with increase in metal thickness but decreases with an increase in enamel thickness. Figure 3 indicates that, although the thermal-shock resistance decreases greatly with enamel thickness, in ranges up to about thirty thousandths above these thicknesses the effect is not pronounced.

VII. Summary

The test method used has proved to be satisfactory and correlates with field experience. The results show that an increase in the thickness of enamel over the commercial range results in a decrease in thermal-shock resistance and that increases in the thickness of the stock have only a slight effect on increasing the thermal-shock resistance.

A study of the character of the failures and the behavior of the ware under test indicates that thermal-shock failures, such as those occurring on kitchenware, are the result of the expansion and contraction of the bottom of the utensil which puts strains in the enamel coating.

Acknowledgment

This investigation was carried out in the Department of Ceramic Engineering at the University of Illinois and was financed by the Enameled Utensil Manufacturers' Council of Cleveland, Ohio.

The authors wish to express their appreciation to George H. Zink, formerly connected with this project for some of the early work he did in connection with the development of a thermal-shock test and to the members of the Technical Committee of the Council, E. C. Dexheimer, H. C. Arnold, E. H. Kelsey, B. S. Kirk, P. A. Mallonn, and A. J. Vollrath for their advice, suggestions, and cooperation.

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EFFECT OF TEMPERATURE ON HOMOGENIZING RATE OF SODA-LIME-SILICA GLASS*

By R. L. Tiede and F. V. Tooley

Abstract

Density-spread determinations were made on a series of melts of a soda-lime-silica glass prepared at temperatures ranging from 1232° to 1454°C. for a four-hour period in the absence of furnace refractory and under conditions of minimum convection mixing. A sharp drop in density spread in the range 1232° to 1288°C., a minimum at about 1325°C., and a slowly increasing density spread at temperatures above 1325°C. were observed.

The portion of glass responsible for the major part of the density spread was found to be concentrated in the top half of the glass at both 1232° and 1454°C. At the higher temperature, the improvement in the homogeneity of the bottom layer was more marked than that observed in the top layer as compared with the results obtained on the lower-temperature melt. The density spread of the glass in the bottom layer in the case of the high-temperature melt was in the range of that observed for commercial soda-lime-silica glass of good quality.

A possible explanation for the observed increase in density spread at higher temperatures (above 1325°) is offered on the basis of more rapid initial segregation during melting at higher temperature as inferred from the density-spread data and from chemical analyses of the glass from the top and bottom portions of melts made at 1232° and 1454°C.

Loss in weight of the glass due to volatilization was determined at 1232° and at 1454°C. and was found to amount to less than 0.01% for a four-hour melting period at both temperatures.

Moderate mixing, achieved by repeated cracking and remelting of the glass and by melting in a rotating tilted crucible, had a marked effect in lowering the density spread.

The data afforded by these experiments lend further emphasis to the view that convection currents in commercial tank operation are highly significant in improving the homogeneity of a soda-lime-silica glass.

I. Introduction

In an earlier paper,[1] the authors presented the results of an investigation of the rate of homogenizing of a soda-lime-silica glass under conditions of minimum convection mixing and in the absence of refractory materials. This work was carried out on samples melted at a constant temperature, and the degree of homogeneity measured by the centrifuge technique was expressed in terms of density spread as a function of time. It was found that the density spread decreased rapidly during the first 16 hours of melting at 1400°C. (a drop of 9°C. in density spread) following which further decrease occurred at a much slower rate, amounting to but an additional 6°C. drop in density spread from the sixteenth to the sixty-fourth hours. It was also found that the portion of glass responsible for the major part of the density spread was a light fraction, which tended to form or accumulate at the surface of the melts.

The present investigation is a continuation of this former work and is concerned with the change of degree of homogeneity of a soda-lime-silica glass with respect to temperature.

The method and apparatus and the experimental procedure employed were the same as those used in the earlier work and need not be repeated here.

II. Interpretation of Density-Spread Data

It is appropriate to discuss in some detail the theory underlying the interpretation of density-spread data and to point out in general the value and limitations of the method in such a study. Two factors which should be considered in the interpretation of density-spread data are (1) the density spread itself and (2) the shape of the curve. It is to be remembered that the total density spread obtained is independent of the relative amounts of glass of different densities giving rise to this spread. Therefore, when an increase or decrease in density spread is observed, it must be interpreted to be due to a change in composition of the inhomogeneity with respect to the parent glass and not as a change in amount of inhomogeneity present.

The curves represented in Fig. 1 are idealized curves which illustrate the situations normally encountered; any situation can be represented by some combination of these curves. Figure 1 (*A*) represents an example in which all of the particles are of nearly the same density as in the case of good optical glass. With reference to the extent to which a high degree of homogeneity can be inferred from a low density spread, the reader is cautioned that the latter refers only to den-

* Presented at the Forty-Sixth Annual Meeting, The American Ceramic Society, Pittsburgh, Pa., April 5, 1944 (Glass Division). Received April 19, 1944.

[1] F. V. Tooley and R. L. Tiede, "Factors Affecting Degree of Homogeneity of Glass," *Jour. Amer. Ceram. Soc.*, **27** [2] 42–45 (1944).

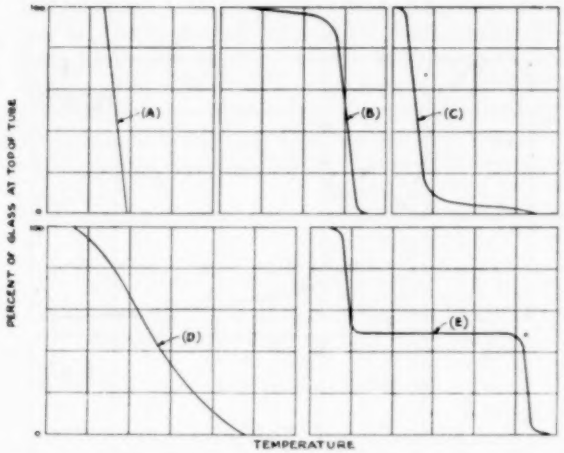

FIG. 1.—Idealized density distribution curves illustrating situations normally encountered.

sity gradient, and inference of homogeneity from this property is based only on the improbability of the coexistence of glasses differing in composition but equal in density.

That there may be instances encountered in which no such "improbability" exists is illustrated by Morey's composition-isodensity diagram for a portion of the Na_2O–CaO–SiO_2 system.[2] In the supposition that soda is being lost from a glass surface by volatilization, the change in composition at the surface will occur along a straight line passing through the 100% Na_2O apex and the original composition (providing some other influence does not alter the ratio of CaO and SiO_2). It is apparent that in certain regions of composition (for example, CaO = 30%, SiO_2 = 55.0%, Na_2O = 15%) this line tends to coincide with an isodensity line, and in such a region actual changes in glass composition would not be detected by the density spread. In the present study, the region of composition was such that a coincidence of this kind would not logically be expected.

Another possibility giving rise to a low density spread is that the inhomogeneity may be so fine or so well distributed that density differences observed between individual particles are not representative of the density difference between the inhomogeneity and matrix glass.

Figure 1 (*B*) represents the case in which a small percentage of the particles is higher in density than the parent glass. The inference is that these particles represent a high density cord; conversely, that if a heavy cord exists, this is the type of curve that will result if the cord is of sufficient size to appear as individual particles when the sample is crushed and screened. Figure 1 (*C*) represents the corresponding case for particles of density lower than that of the parent glass. The amount of cord may be estimated from curves of these types.

[2] G. W. Morey, Properties of Glass, Fig. X5, p. 249. Amer. Chem. Soc. Monograph Series, No. 77. Reinhold Publishing Corp., New York, 1938. 561 pp.; *Ceram. Abs.*, **18** [2] 48 (1939).

Figure 1 (*D*) represents a situation that might be interpreted as (1) a case in which a gradual composition gradient rather than a distinct cord exists or (2) a case in which a distinct cord exists which is so finely divided as to render improbable its isolation in separate particles of the size required for the measurement. It will be recalled that some technical difficulties are encountered in the use of particles less than 160- to 200-mesh in size.[3]

Figure 1 (*E*) represents the type of curve that would result from running a mixture of two glasses, each of small density spread but differing in density.

Turnbull and Ghering[3] have discussed the interpretation of the curves obtained on glasses from tank operation when the possibility of inhomogeneities due to refractories and unmelted batch is encountered. The foregoing analysis refers primarily to inhomogeneities arising from incompleted homogenizing in a refractory and batch-free system.

III. Homogeneity of Soda-Lime-Silica Glass with Respect to Temperature

The theoretical composition of the glass used was SiO_2 73.0%, Na_2O 17.0%, and CaO 10.0%; the batch was compounded from commercial potter's flint (95% 200-mesh), calcium carbonate (Diamond Alkali Non-Fer-Al, 95% 200-mesh), and sodium carbonate (Baker and Adamson c.p. powdered). The composition, source, and specification of materials as well as the method of mixing and melting were the same as those used in the earlier work.[1]

The constant time interval observed was four hours; the temperatures varied from 1232° to 1454°C. by 56° increments. Duplicate melts and measurements were made in all cases.

Figure 2 presents the experimental results obtained for the various temperatures employed. It is to be noted that these density-spread values are very high in comparison with values of about 3°C. encountered in commercial glasses. This is a consequence of the short melting time observed and the minimum of convection mixing.

Figure 3 was obtained by plotting the data from Fig. 2 to show density spread as a function of temperature for a constant melting time. The tendency for the density spread to show an increase at the higher temperature is perhaps the most significant experimental result obtained, and the major part of the discussion has to do with a possible mechanism by which such a result might reasonably be explained.

Following the establishment of the curves of Figs. 2 and 3, further work was carried on toward determining the mechanism giving rise to this result. Additional melts were made at 1232° and 1454°C. following the standard procedure of melting and annealing. The glass was removed from the crucibles in large pieces and was separated into two portions by sawing with a diamond saw; one portion represented the top half of the glass from the crucible, the other the bottom half.

[3] J. C. Turnbull and L. G. Ghering, "Cord Analysis," *Jour. Amer. Ceram. Soc.*, **24** [8] 264–70 (1941).
See also footnote 1.

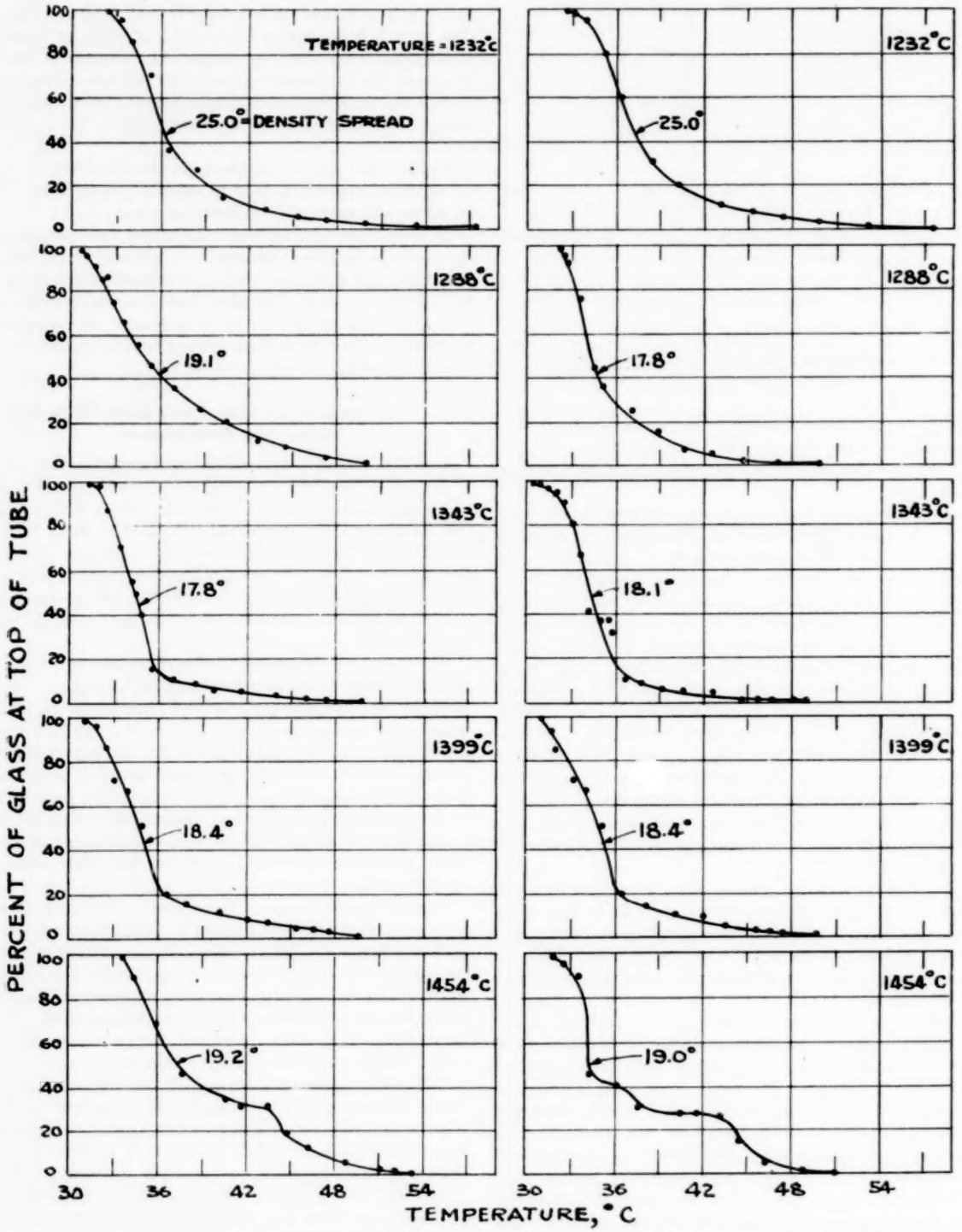

FIG. 2.—Density distribution curves for pairs of glasses prepared at different melting temperatures for constant time intervals (4 hr.); inserted data indicate melting temperatures (°C.) and density spread (°C.).

Density-spread determinations were made on each of the two portions from each of the melts with the results indicated in Fig. 4. At both temperatures, the top glass is seen to account for the major part of the total density spread. Furthermore, at the higher temperature, the improvement in the homogeneity of the bottom layer is more marked than that observed in the top layer as compared with the results obtained on the lower temperature melt. The average density spread of the bottom layer of the 1454°C. melt is but 40% of that of the bottom layer of the 1232°C. melt, while the average density spread of the top layer at the higher temperature is 72% of that of the lower temperature. A point of interest is the fact that the density spread of the lower layer in the case of the high-temperature melt was in the range of that observed for commercial soda-lime-silica glass of good quality.

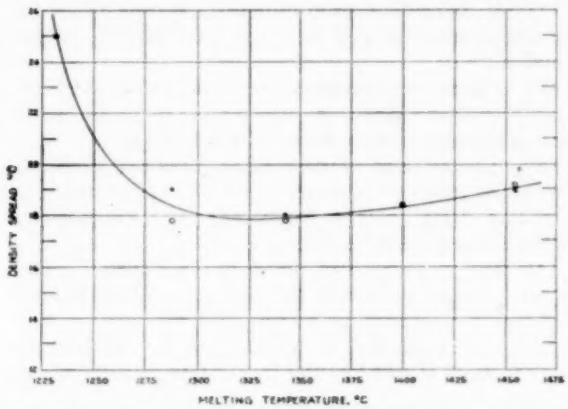

FIG. 3.—Density spread as function of melting temperatures; data same as those of Fig. 2.

Chemical analyses were determined on glass from the top and bottom sections of these melts made at

TABLE I

CHEMICAL ANALYSES ON GLASS FROM TOP AND BOTTOM SECTIONS

	Section		Section	
	Top (1232°C.)	Bottom (1232°C.)	Top (1454°C.)	Bottom (1454°C.)
SiO_2	73.0	72.2	72.9	72.2
Al_2O_3	0.3	0.3	0.3	0.3
CaO	10.0	10.5	9.7	10.5
Na_2O	16.7	16.9	16.8	16.9

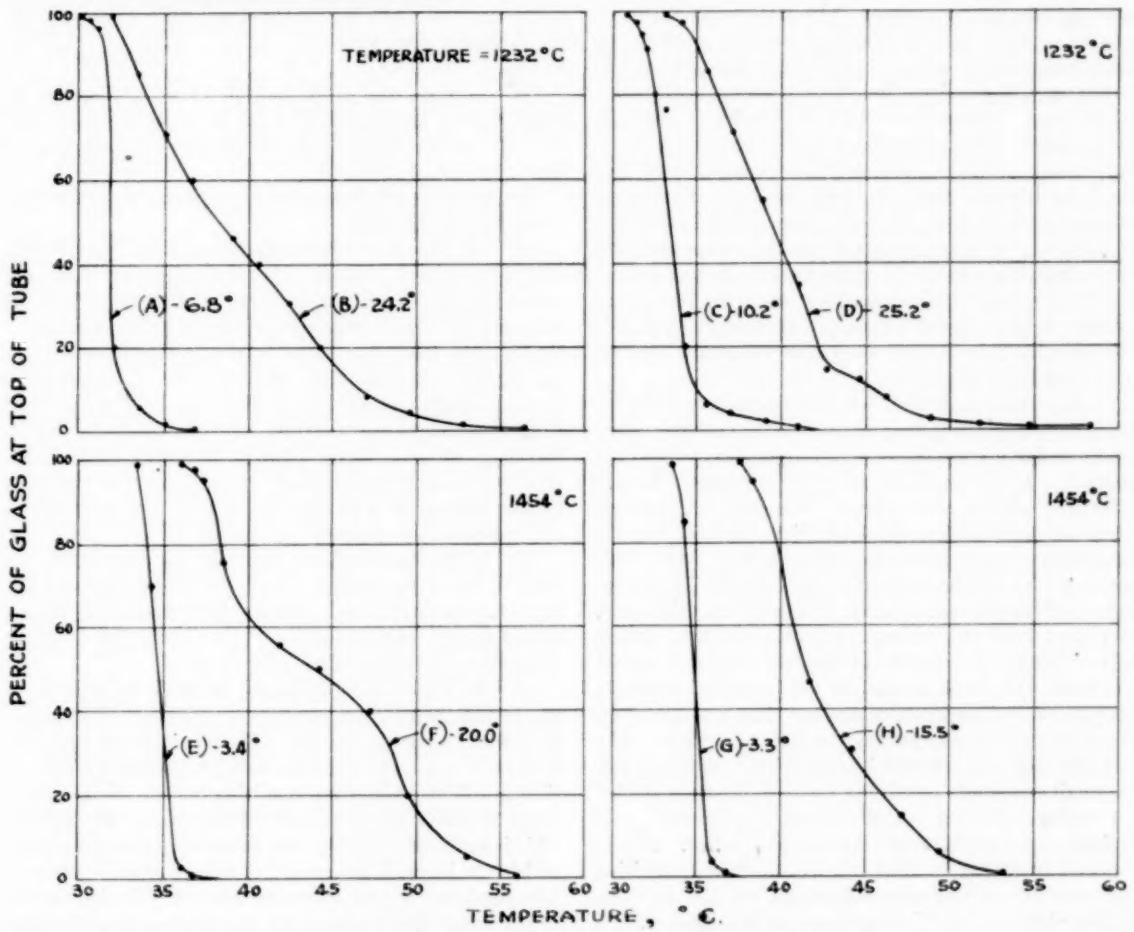

FIG. 4.—Density distribution curves on bottom and top glass from same crucible (duplicate runs); curves (*B*), (*D*), (*F*), and (*H*) resulted from the top portions.

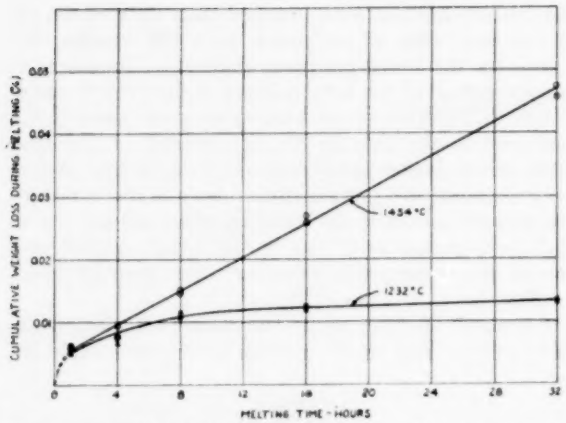

FIG. 5.—Loss of volatile material from melts with respect to time and temperature.

1232° and 1454°C. The results are given in Table I. In examining these data, the analyses indicate that the bottom section of the sample melted at 1232°C. had the same composition as the bottom section of the sample melted at 1454°C. and that the top sections of the two melts were also quite similar. The major differences in composition between the top and bottom sections at both temperatures were in the SiO_2 content, which was higher in the top section of both melts, and in the CaO content, which was lower. The Na_2O content also appeared to be somewhat lower in the top section.

A further piece of pertinent information was furnished by determining the rate of loss of volatile material, presumed to be soda, from melts at 1232° and 1454°C. It was impossible to determine the rate of volatilization accurately under exactly the same conditions observed during melting because the large crucibles were difficult to weigh accurately and because of refractory pickup from the walls and bottom of the resistance furnace.

The data shown in Fig. 5 were obtained as follows: A batch of about 300 gm. was melted at 1400°C. long enough to form completely batch-free glass (about 45 minutes). This glass was removed, crushed to pass an 8-mesh screen, and mixed. Portions of approximately 50 gm. (the amount of glass melted for the homogeneity runs) were placed in shallow pure platinum crucibles of the same diameter as the large crucibles used in the other melts. These crucibles were introduced into the furnace by placing them inside another platinum crucible of slightly larger diameter and about the same height as the larger crucible in which the other melts were made. The two crucibles were separated by means of a fused alumina disk. The outer crucible was covered loosely with a platinum lid. The small crucibles containing the samples were cooled in a desiccator after removal from the furnace, and weighings were made on the analytical balance. It is to be noted from Fig. 5 that, for the four-hour melting time observed in these investigations, the loss of volatile material from the glass amounts to less than 0.01% at both 1232° and 1454°C. and that very little difference was observed between the results at these two temperatures. For longer melting periods, the difference is more pronounced.

IV. Interpretation and Discussion

An examination of the data brings out the following points:

(1) An immediate drop in density spread occurs in the temperature interval from 1232° to 1288°C. (Figs. 2 and 3).

(2) The density spread reaches a minimum at about 1325°C., after which it apparently increases with further increase in temperature (Figs. 2 and 3).

(3) The amount of cord (glass of lower density) appears to reach a minimum at 1343°C., after which it increases with further increase in temperature, markedly so at 1454°C. (Fig. 2).

(4) The major part of the glass responsible for the density spread occurs in the top layer in both low- and high-temperature melts (Fig. 4).

(5) The tendency to homogenize in the bottom layer is more marked in the higher temperature melts (Fig. 4).

(6) Chemical analyses show that there is a tendency for concentration of SiO_2 in the top layer of glass in the melts and of CaO in the bottom; this effect is approximately the same at either 1232° or 1454°C. (Table I).

(7) Volatile loss from molten glass appears to be small during the four-hour time interval observed and over the temperature range investigated, amounting to less than 0.01% (Fig. 5).

On the basis of these data, the mechanism may be visualized as follows:

(*a*) At the lower temperatures (1232° to 1288°), diffusion mixing begins to overcome the first inhomogeneous condition caused by the formation of eutectic or other low-temperature liquids and their segregation from the more refractory components of the batch. A silica-rich surface layer is established because lower density glass migrates to the top and silica particles are buoyed up by bubbles during melting. A lower layer likewise is established, which is rich in CaO, presumably because of the draining to the bottom of a heavier fraction of the melt under the influence of gravity.

(*b*) In the intermediate temperature zone (1288° to 1343°), all of the things occur that take place in the lower temperature zone plus an increase in rate of diffusion mixing and in fluidity. The net result of these effects is a decrease in density spread.

(*c*) At higher temperatures, increase in fluidity in the initial melting accentuates segregation of the type described in paragraph (*a*). This segregation proceeds in such a way as to produce a slightly greater composition gradient than that resulting in the temperature range corresponding to the minimum density spread. This is indicated both by the increase in density spread and in the increase in amount of inhomogeneity present. The tendency for an increased rate of diffusion mixing at the same time is shown by the marked improvement observed in the glass from the bottom half of the melt.

Data from a previous paper[1] would indicate that dif-

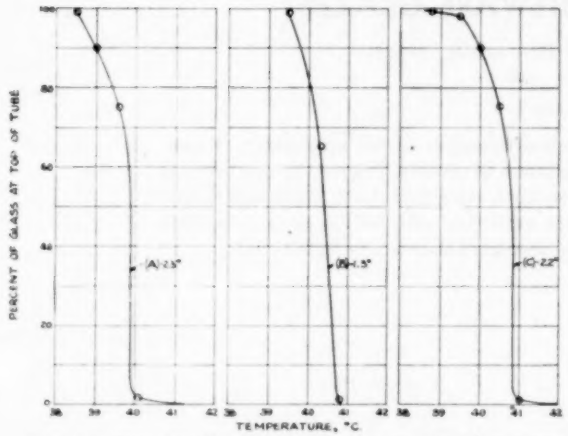

FIG. 6.—Density distribution curves on glass homogenized by repeated cracking and remelting (curves (*A*) and (*B*)) and by mixing in rotating, tilted furnace (curve (*C*)).

fusion mixing would eventually overcome the effect of initial segregation during melting because there is a continuous decrease in density spread for a period of 64 hours at 1400°C.

It should be noted that the analytical data presented give only the average analyses of the glass from the top and bottom sections of the melts. The results show clearly that segregation has taken place, thus corroborating the density-spread observations made; they give no indication, however, of the relative density spread of the top sections in the two cases, since the amount and composition of cord may be much different in one case than in the other.

It is also significant to observe the result on density spread achieved by moderate mixing when (1) the glass was taken through several cycles of crushing and remelting and (2) the glass was melted in a rotating crucible in a tilted furnace similar to that described by Potts, Brookover, and Burch in a recent paper.[4]

The results of these experiments are indicated in Fig. 6. These measures were quite effective in reducing the spread. Curves (*A*) and (*B*) resulted from measurements on glasses prepared by observing three cycles of melting for one hour at 1400°C., cooling, crushing to pass an 8-mesh screen, and remelting. The total melting time was four hours. Curve (*C*) was obtained on glass prepared by melting the batch for four hours at 1400°C. in a resistance furnace designed so as to rotate the crucible at $1^1/_3$ r.p.m. with its axis inclined 12 degrees from the vertical.

The point of view was expressed in a previous paper[1] that "temperature, time, and convection mixing characteristic of a tank operation, in comparison with the experimental conditions observed herein, are very effective in improving homogeneity, especially when a dehomogenizing tendency caused by the refractories is also present in the tank operation." The present data involving the temperature factor together with the data afforded by the foregoing mixing experiments would seem to lend further emphasis to the view that convection currents in a tank operation are highly significant and possibly the most significant factor in promoting the homogeneity of a soda-lime-silica glass. It is assumed in this connection that convection stirring would serve the same end as that achieved by the simple mixing experiments described.

[4] J. C. Potts, George Brookover, and O. G. Burch, "Melting Rate of Soda-Lime Glasses as Influenced by Grain Sizes of Raw Materials and Additions of Cullet," *Jour. Amer. Ceram. Soc.*, **27** [8] 225–31 (1944).

V. Summary

(1) Density-spread determinations were made on a series of melts of a soda-lime-silica glass prepared at temperatures ranging from 1232° to 1454°C. for a four-hour period in the absence of furnace refractory and under conditions of minimum convection mixing. A sharp drop in density spread in the range 1232° to 1288°C., a minimum at about 1325°C., and a slowly increasing density spread at temperatures above 1325°C. were observed.

(2) The portion of glass responsible for the major part of the density spread was found to be concentrated in the top half of the glass at both 1232° and 1454°C. At the higher temperature, the improvement in the homogeneity of the bottom layer is more marked than that observed in the top layer as compared with the results obtained on the lower-temperature melt. The density spread of the glass in the bottom layer in the case of the high-temperature melt was in the range of that observed for commercial soda-lime-silica glass of good quality.

(3) A possible explanation for the observed increase in density spread at higher temperature (above 1325°) is offered on the basis of more rapid initial segregation during melting at higher temperatures as inferred from the density-spread data and chemical analyses of the glass from the top and bottom portions of melts made at 1232° and 1454°C.

Loss in weight of the glass due to volatilization was determined at 1232° and at 1454°C. and was found to amount to less than 0.01% for a four-hour melting period at both temperatures.

(4) Moderate mixing achieved by repeated cracking and remelting of the glass and by melting in a rotating, tilted crucible has a marked effect in lowering the density spread.

The data afforded by these experiments lend further emphasis to the view that convection currents in commercial tank operations are highly significant in improving the homogeneity of a soda-lime-silica glass.

Acknowledgment

The authors wish to express their appreciation to H. H. Gregg of this laboratory who obtained the analytical data and to O. W. Metcalf for his assistance with the experimental work reported herein.

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RAW LEADLESS WHITEWARE GLAZES*

By C. G. Harman and Howard R. Swift

Abstract

A study was made of the effect of composition changes on the appearance of raw, leadless, boron-free glazes. The approximate limits of composition for the most fusible glazes of this type were found after varying the CaO, BaO, SrO, ZnO, MgO, and KNaO contents. Alumina and silica variations were made for some of the more promising glazes. Some general remarks concerning raw leadless glazes are included.

I. Introduction

The popularity of lead borosilicate glazes in the whiteware industry is due to the convenient maturing temperature, long maturing range, and good gloss. These advantages have been sufficient to outweigh some of the disadvantages of this type of glaze, the most outstanding of which are the presence of the poisonous lead and characteristic surface imperfections. Attempts to develop leadless glazes have usually met difficulties from the aspects of both fusibility and glaze fit.

II. Review of Literature

Raw leadless glaze compositions maturing as low as cone 04 have been described in the literature. Boric acid,[1] cryolite,[2] colemanite,[3] and lithium carbonate[4] are common ingredients in these glazes. The high alkali content, characteristic of these glazes, has limited their application to the whiteware industry.

Some experimental work on low-maturing, raw, leadless glazes has been in progress in this laboratory from time to time for several years. Hanks[5] produced a satisfactory cone 6 glaze by fixing the lower limit of alkali and the upper limit of alkaline earths and their relative amounts. Figure 1 summarizes briefly some of his results. The CaO, ZnO, and BaO contents were varied, keeping constant the 0.2 equivalent of alkali and 0.2 equivalent of MgO. He and previous investigators found the alumina-silica ratio of 1 to 10 to be satisfactory. The best glazes were those with 0 to 0.2 equivalent of CaO, 0 to 0.2 equivalent of ZnO, and 0.1 to 0.5 equivalent of BaO.

In another series of raw glazes of similar composition, Hanks[5] varied the CaO, MgO, and ZnO contents,

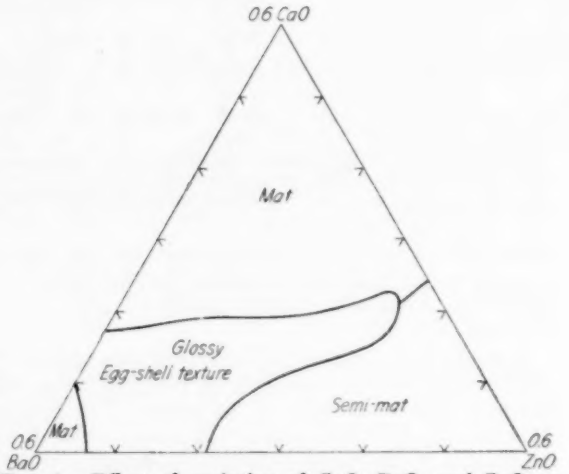

FIG. 1.—Effect of variation of CaO, BaO, and ZnO on appearance of raw glazes fired to cone 1.

$$\left.\begin{matrix}0.2\ \text{KNaO}\\0.2\ \text{MgO}\\0.6\begin{cases}\text{CaO}\\\text{BaO}\\\text{ZnO}\end{cases}\end{matrix}\right\}0.3\ Al_2O_3\quad 3.0\ SiO_2$$

keeping the BaO and the alkali constant. The results are shown in Fig. 2. The best glazes contained 0 to 0.1 equivalent of MgO, 0.2 to 0.3 equivalent of CaO, and 0.2 to 0.3 equivalent of ZnO. Further work with glaze A (Fig. 2) showed that it, as others in the series, had to be very finely ground before it could be classified as satisfactory at cone 4. It was apparent from these investigations that cone 4 was the minimum maturing temperature for raw, leadless, boron-free glazes containing CaO, MgO, ZnO, and BaO.

III. Scope of Investigation

On the basis of available information, strontia would be expected to act not only to lower the maturing temperature of this type of glaze but to impart other desirable characteristics as well. It was the purpose of this investigation to extend the work started by Hanks to include SrO and to investigate the limits of composition and the general characteristics of the resulting glazes.

In the first part of this investigation, the alkali content was held constant at 0.2 equivalent; in the second part, it was entirely removed. Variations of CaO, BaO, SrO, ZnO, and MgO were studied. Alumina and silica variations were made with the more promising glazes.

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* Presented at the Forty-Sixth Annual Meeting, The American Ceramic Society, Pittsburgh, Pa., April 5, 1944 (White Wares Division). Received October 2, 1944.

[1] K. M. Kautz, "Effect of Boric Acid in Raw Milled Glazes," *Jour. Amer. Ceram. Soc.*, **15** [11] 638–43 (1932).

[2] M. M. French, "Colemanite as Glaze Material," *ibid.*, **14** [10] 739–41 (1931).

[3] (*a*) C. W. Merritt, "Raw Leadless Glazes at Low Temperatures," *Bull. Amer. Ceram. Soc.*, **14** [3] 104–106 (1935).

(*b*) Düpmann, "Raw Leadless Glazes at Low Temperatures," *Keram. Rund.*, **43**, 445–46 (1935).

See also French, footnote 2.

[4] F. W. Richardson, "Use of Lithium Carbonate in Raw Alkaline Glazes," *Jour. Amer. Ceram. Soc.*, **22** [2] 50–53 (1939).

[5] C. F. Hanks, "Substitution of Barium for Lead in a Raw Glaze." Bachelor of Science Thesis, University of Illinois, Urbana, Ill., 1940 (unpublished).

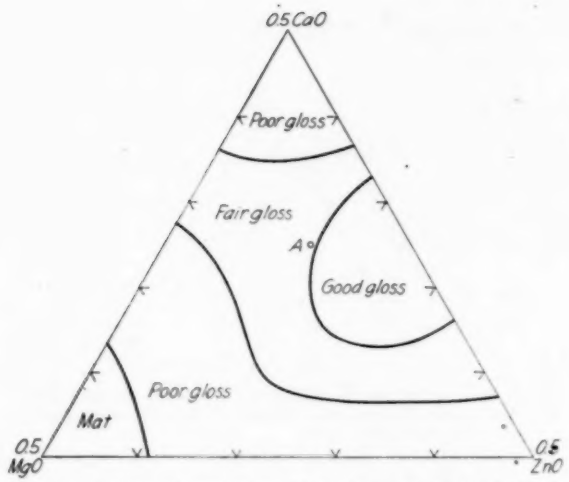

FIG. 2.—Effect of variation of CaO, ZnO, and MgO on appearance of raw glazes fired to cone 4+.

0.2 KNaO
0.3 BaO
0.5 (CaO, MgO, ZnO) } 0.3 Al_2O_3 3.0 SiO_2

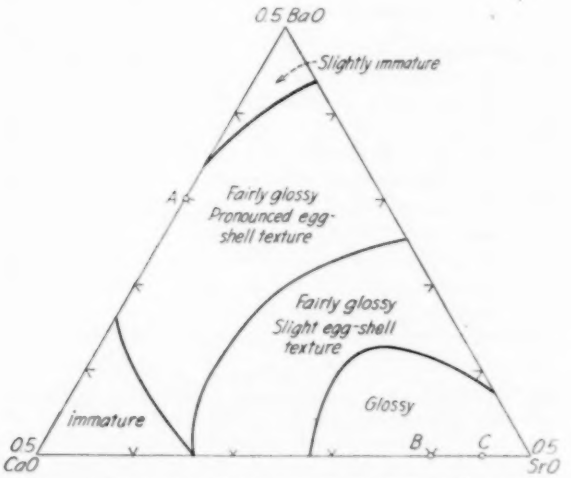

FIG. 3.—Effect of variation of CaO, BaO, and SrO on appearance of raw glazes fired to cone $1^1/_2$.

0.2 KNaO
0.15 ZnO
0.05 CaO
0.1 MgO } 0.3 Al_2O_3 3.0 SiO_2
0.5 (CaO, BaO, SrO)

IV. Effect of Composition Changes on Appearance of Raw Leadless Glazes Containing 0.2 Equivalent of Alkali

(*A*) The effect of varying BaO, CaO, and SrO on the appearance of a series of raw glazes fired to cone $1^1/_2$ is indicated in Fig. 3. Glazes high in strontia were superior in gloss and surface texture to the other glazes in the field but were inferior to the conventional fritted glazes in both respects.

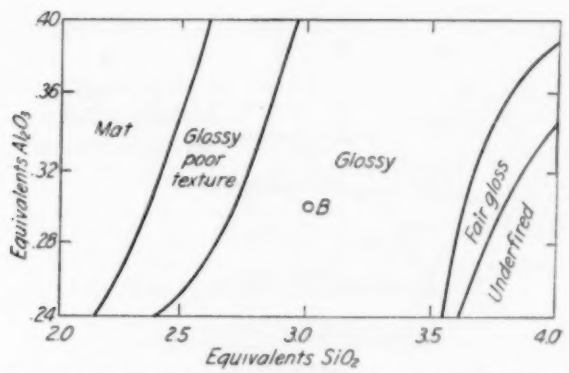

FIG. 4.—Alumina-silica variations with constant RO fired to cone 1.

0.20 KNaO
0.15 CaO
0.15 ZnO
0.10 MgO
0.40 SrO } 0.24–0.40 Al_2O_3 2.0–4.0 SiO_2

FIG. 5.—Effect of variation of MgO, ZnO, and SrO on appearance of raw glazes fired to cone 01.

0.20 KNaO
0.10 CaO
0.10 ZnO
0.30 SrO } 0.3 Al_2O_3 3.0 SiO_2
0.30 (MgO, ZnO, SrO)

(*B*) The effect of varying the alumina and silica of a glaze having the RO composition of glaze B (Fig. 3) is shown in Fig. 4. The range of glossy glazes was quite large, extending from 0.24 equivalent of alumina and 2.5 equivalents of silica to 0.40 equivalent of alumina and 4.0 equivalents of silica. Additions of alumina and silica reduced the tendency to craze and impaired the gloss slightly.

(*C*) The effect of varying the amounts of MgO, ZnO, and SrO on the appearance of a series of raw glazes fired to cone 01 is shown in Fig. 5. Glaze C of this field has the same composition as glaze C of Fig. 3. Over 0.05 equivalent of MgO markedly increased the refractoriness. The lowest maturing glaze in this field, indicated as glaze D, had the following composition:

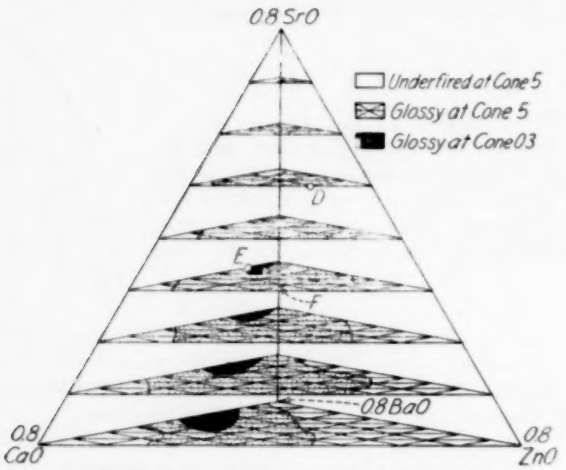

FIG. 6.—Effect of varying SrO, BaO, CaO, and ZnO on appearance of raw leadless glazes.

0.2 KNaO
0.8 { BaO / SrO / CaO / ZnO } 0.3 Al_2O_3 3.0 SiO_2

0.2 KNaO
0.1 CaO
0.2 ZnO
0.5 SrO
} 0.3 Al_2O_3 3.0 SiO_2

This glaze tended to craze when applied on a dinnerware body and showed minor surface imperfections when fired to cones 01 to 3.

(*D*) A four-component field was made, varying the CaO, BaO, SrO, and ZnO contents to define the exact limits of alkaline earths The alkali was held constant at 0.2 equivalent and the alumina and silica at 0.3 and 3.0 equivalents, respectively. The appearance of these glazes, when fired to cones 03 and 5, is indicated in Fig. 6.

The most fusible composition in this field, indicated as glaze E, Fig. 6, had the following composition:

0.2 KNaO
0.3 SrO
0.4 BaO
0.1 CaO
} 0.3 Al_2O_3 3.0 SiO_2

This glaze was quite glossy when fired as low as cone 03 and was satisfactory in most respects even when fired as high as cone 10. The glaze tended to craze when applied on some bodies but not on others. The most fusible glazes in this field had the approximate limits of composition as follows:

0.2 KNaO
0.3–0.5 BaO
0.0–0.3 CaO
0.0–0.1 ZnO
0.0–0.4 SrO
} 0.3 Al_2O_3 3.0 SiO_2

(*E*) The effect of varying alumina and silica on the appearance of the most fusible glaze from the preceding field, glaze E, is shown in Fig. 7. Additions of alumina and silica decreased the crazing tendency for this glaze but also decreased the gloss and made slight surface imperfections more pronounced.

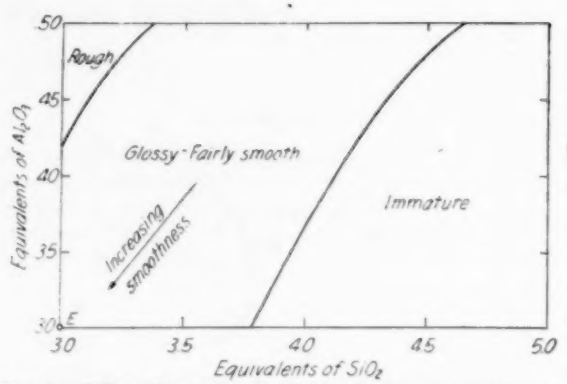

FIG. 7.—Effect of varying alumina and silica on appearance of a low-temperature raw, leadless glaze fired to cone 4.

0.2 KNaO
0.1 CaO
0.3 SrO
0.4 BaO
} 0.3–0.5 Al_2O_3 3.0–5.0 SiO_2

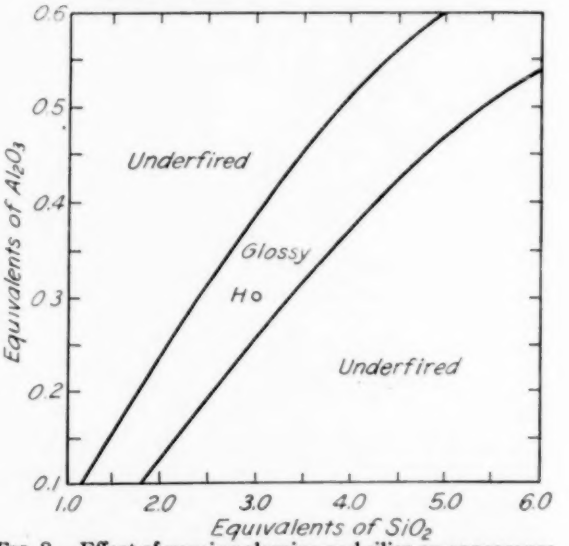

FIG. 8.—Effect of varying alumina and silica on appearance of a strontia-alumina-silica glaze fired at cone 11.

1.0 SrO 0.1–0.6 Al_2O_3 1.0–6.0 SiO_2

(*F*) A study was made of the effect of grinding time and the effect of variations in suspending agents on the appearance of a raw leadless glaze (glaze D) in order to improve the surface texture and craze resistance. With finely milled glazes, it was possible to get more silica into solution thereby lowering the coefficient of expansion. Finely milled glazes matured at a lower temperature than coarser glazes and had a superior surface texture. Variation in the quantity and type of suspending agents had little effect on the appearance of the fired test specimens except that a minimum amount of suspending agent appeared to be the most desirable.

V. Effect of Composition Changes on Appearance of Alkali-Free Raw Leadless Glazes

(*A*) A concurrent investigation was conducted on the use of strontia in simple glazes for the purpose of further studies on the action of strontia and its possibilities

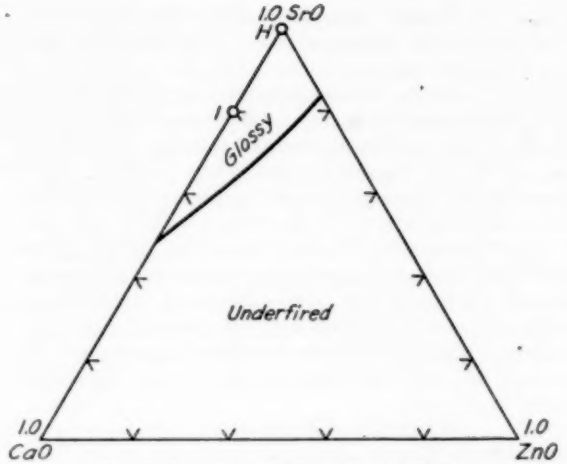

FIG. 9.—Effect of varying SrO, CaO, and ZnO on appearance of an alkali-free glaze fired to cone 11.

$$\left.\begin{matrix}\text{SrO}\\ 1.0\ \text{CaO}\\ \text{ZnO}\end{matrix}\right\} 0.3\ Al_2O_3\quad 3.0\ SiO_2$$

in special glazes. The effect of varying alumina and silica on the appearance of a strontia-alumina-silica glaze is shown in Fig. 8. Glossy glazes were found with the silica varying from 1.5 to 6.0 equivalents and the alumina varying, at the same time, from 0.1 to 0.6 equivalent when the pieces were fired to cone 11.

(*B*) The effect of varying CaO, ZnO, and SrO on the appearance of one of the glazes from the preceding field (glaze H) is shown in Fig. 9. The gloss was slightly improved with the addition of 0.2 equivalent of CaO; the addition of ZnO made the glazes more refractory.

(*C*) The effect of varying BaO, MgO, and SrO on the appearance of the most fusible glaze from the preceding field (glaze I) is shown in Fig. 10. All of the glazes in this field were glossy when fired to cone 8. When the glazes were fired to cone 02, the lowest maturing composition in this field was readily found. This glaze, designated as glaze J, had the following composition:

$$\left.\begin{matrix}0.2\ \text{CaO}\\ 0.3\ \text{SrO}\\ 0.5\ \text{BaO}\end{matrix}\right\} 0.3\ Al_2O_3\quad 3.0\ SiO_2$$

(*D*) The effect of varying alumina and silica on the appearance of the above glaze (glaze J) is shown in Fig. 11. Only small additions of alumina and silica could be made if the glazes were fired to cone 8. When the glazes were fired to cone 11, however, the range of alumina and silica was extended to include compositions with 0.70 equivalent of alumina and 6.0 equivalents of silica. Only the glazes with low alumina and silica showed any tendency toward crazing when applied on a sanitary-ware body.

VI. Lowest Maturing Raw Leadless Glazes

The lowest maturing raw, leadless, boron-free glaze found in this investigation had the following composition:

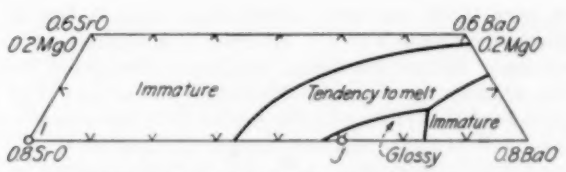

FIG. 10.—Effect of varying SrO, BaO, and MgO on appearance of an alkali-free glaze fired to cone 02.

$$\left.\begin{matrix}0.2\ \text{CaO}\\ 0.6\text{–}0.8\ \text{SrO}\\ 0.6\text{–}0.8\ \text{BaO}\\ 0.2\text{–}0.0\ \text{MgO}\end{matrix}\right\} 0.3\ Al_2O_3\quad 3.0\ SiO_2$$

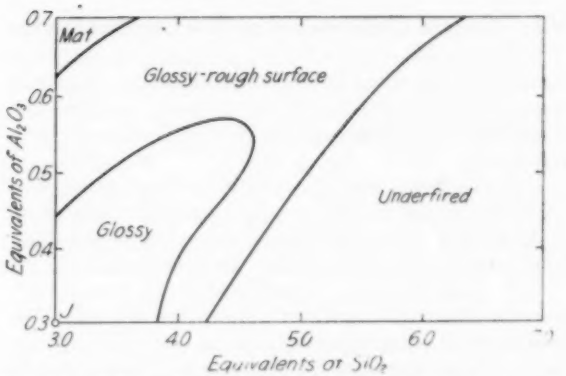

FIG. 11.—Effect of varying alumina and silica on appearance of an alkali-free glaze fired to cone 8.

$$\left.\begin{matrix}0.3\ \text{SrO}\\ 0.2\ \text{CaO}\\ 0.5\ \text{BaO}\end{matrix}\right\} 0.3\text{–}0.7\ Al_2O_3\quad 3.0\text{–}7.0\ SiO_2$$

$$\left.\begin{matrix}0.2\ \text{KNaO}\\ 0.3\ \text{SrO}\\ 0.1\ \text{CaO}\\ 0.4\ \text{BaO}\end{matrix}\right\} 0.3\ Al_2O_3\ 3.0\ SiO_2$$

	(%)
Barium carbonate	22.1
Calcium carbonate	2.7
Strontium carbonate	11.6
Nepheline syenite	25.3
Tenn. ball clay No. 5	2.2
Pyrophyllite	6.0
Flint	30.1

This glaze started to mature at cone 03 and was not overfired at cone 10. The surface was quite smooth although not quite so glossy as lead borosilicate glazes. A slight tendency to craze on some bodies was reduced by firing to a higher temperature or by increasing the alumina to 0.4 equivalent and the silica to 4.0 equivalents. The gloss was reduced somewhat by this change. Fine grinding was essential for this type of glaze and the clay had to be reduced to 0.03 equivalent (about 2%) to reduce application defects. In an experiment on the effect of glaze composition on ten underglaze colors, every color was superior with the raw leadless glaze as compared with a lead borosilicate glaze.

The lowest maturing alkali-free glaze found in this investigation had the following composition:

$$\left.\begin{matrix}0.3\ \text{SrO}\\ 0.2\ \text{CaO}\\ 0.5\ \text{BaO}\end{matrix}\right\} 0.3\ Al_2O_3\quad 3.0\ SiO_2$$

This glaze showed some tendency toward maturing

at cone 02, it was still underfired at cone 5, but it matured at cones 7 to 11. At cone 12, it showed some tendency toward overfiring, which was eliminated by the addition of magnesia or alumina and silica. The glaze tended to craze on a dinnerware body when underfired, but properly matured samples did not show this tendency. Underglaze colors did not run or alter in appearance with this glaze.

It may be of interest to note that the alkaline earths are approximately in the same ratio in the lowest maturing alkali-free glaze as they are in the lowest maturing glaze containing 0.2 equivalent of alkali.

VII. General Observations on Raw Leadless Glazes

(1) No more than 0.05 equivalent of magnesia should be introduced in raw leadless glazes; magnesia apparently does not have time to react to lower the coefficient of expansion of the glaze and acts only as a refractory.

(2) In low-temperature, raw, leadless glazes, zinc oxide should not be introduced in over 0.2 equivalent; it does lower the coefficient of expansion of the glaze somewhat, but it also increases the refractoriness.

(3) A substitution of barium oxide for lime in raw, leadless glazes gives greater fluidity and increases the coefficient of expansion; baria is an essential flux, but because of the increased expansion of the glaze, amounts of more than 0.5 equivalent may cause crazing.

(4) Beryllium oxide increases the refractoriness of this type of glaze.

(5) No benefits were derived from the use of lithia even though the feldspars were in the ratio of their lowest melting mixture.

(6) Nepheline syenite promotes early vitrification and is preferable to feldspar for this type of glaze.

(7) Fine grinding is essential in order to facilitate the solution of the silica; either fine grinding of the quartz alone or the quartz plus nepheline syenite produces the same effect.

(8) Strontia is essential because it increases the fusibility of the glazes and does not increase the expansion as much as baria; larger ranges of alumina and silica appear to be possible with the strontia glazes.

(9) Underglaze colors are much more stable in contact with the raw leadless glazes than with lead-borosilicate glazes.

(10) Raw leadless glazes are characterized by an exceptionally long firing range.

Acknowledgment

This investigation was conducted in the Department of Ceramic Engineering at the University of Illinois as a cooperative research project between the Engineering Experiment Station and the Barium Reduction Corporation of South Charleston, W. Va. The authors wish to express their gratitude to J. D. Griffith and E. P. Murphy for their assistance in the laboratory.

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STUDY OF GLAZE PENETRATION AND ITS EFFECT ON GLAZE FIT: I–III*

By Everett Thomas, Milton A. Tuttle, and Esther Miller

Abstract

A method for determining glaze penetration was developed and the effect of glaze penetration on glaze fit studied. The effects of twenty-four fluxes on penetration of a base glaze into semivitreous, hotel china, terra cotta, cordierite, pyrophyllite, wall tile, and steatite bodies were determined. The result shows that glaze penetration affects glaze fit and that penetration varies greatly, depending on glaze composition and the character of the body.

I DEVELOPMENT OF TEST FOR PENETRATION

I. Introduction

The manner of adherence and the strains in a glaze are the most important factors in glaze fit. Both are affected by the physical and chemical reactions occurring at the glaze-body interface during firing. This being true, it becomes important to determine how various oxides affect such reactions as well as their effect on glaze fit.

A review of pertinent literature reveals numerous references to the importance of both physical and chemical reactions at the glaze-body interface on glaze fit. In referring to reactions occurring at the glaze-body interface, such terms have been mentioned as "intermediate composition zone," "interfacial layer," "interfacial crystal zone," and "interfacial zone." Statements also have been made to the effect that "the body is dissolved by the glaze," "the glaze penetrates the body," "the glaze acts on the body," "the rate of solution of body by glaze varies with body and glaze composition," "there is an interfacial reaction," "there is a gradual transition from body to glaze," and "there is crystalline growth at the interface."

Schramm,[1] in a study of washes applied on the body under the glaze, found that a glaze is definitely affected by the material upon which it is applied. Hall[2] found

* Presented at the Forty-Fifth Annual Meeting, The American Ceramic Society, Pittsburgh, Pa., April 20, 1943 (White Wares Division). Received October 27, 1943; revised paper received December 4, 1944.

[1] Edward Schramm, "Symposium on Glazes: Problems in Whiteware Glazes," *Bull. Amer. Ceram. Soc.*, **17** [11] 436–40 (1938).

[2] F. P. Hall, "Influence of Chemical Composition on Physical Properties of Glazes," *Jour. Amer. Ceram. Soc.*, **13** [3] 182-99 (1930).

that glazes could be robbed of certain ingredients. There are, however, no data establishing any direct relationship between such reactions and glaze fit.

A study of all the reactions and changes occurring at the glaze-body interface would be extremely complex. The present study will be limited to "glaze penetration." No particular attention will be given to the solution of the body by the glaze or to the development of a crystal layer.

Glaze penetration is defined as the entrance of the glaze into the body by physical or chemical means. This study was undertaken to determine in what manner and to what degree glaze penetration affects glaze fit and the effect of different fluxes on such penetration.

II. Experimental Procedure

The first problem was to develop a test that would measure glaze penetration. Various methods were considered such as microscopic examination, the use of fluorescent glazes, the effect on refractoriness of the body, the use of the spectrograph, and the effect on glaze hardness. The methods that showed most promise were (1) the effect on the refractoriness of the body and (2) the use of the spectrograph. The former method proved more immediately applicable and was used throughout the study. It was not until near the end of the study that a fairly satisfactory spectrograph technique was developed.

(1) Sag Test

Preliminary studies relative to the effect of glaze penetration on the refractoriness of a body were made by using sag bars, 7 in. long, 0.75 in. wide, and 0.10 in. thick. The bars were made of a semivitreous body that contained flint 35, Edgar plastic kaolin 12, No-Karb clay 12, Ky. No 4 ball clay 18, C & C ball clay 10, and Buckingham feldspar 13 parts.

Raw and bisqued (cone 9) sag bars were glazed with a lead and a borosilicate glaze, the formulas for which were as follows:

Lead glaze

$$\left.\begin{matrix}0.090\ K_2O\\0.140\ Na_2O\\0.445\ CaO\\0.325\ PbO\end{matrix}\right\}0.30\ Al_2O_3\quad 2.8\ SiO_2$$

Boron glaze

$$\left.\begin{matrix}0.090\ K_2O\\0.140\ Na_2O\\0.445\ CaO\end{matrix}\right\}0.30\ Al_2O_3\ \left\{\begin{matrix}2.8\ SiO_2\\0.325\ B_2O_3\end{matrix}\right.$$

These glazes were selected because they were known to have equal P.C.E. values and similar fluidity during firing.

The glazed specimens were placed on refractory knife edges $4\frac{1}{2}$ in. apart and were fired to cone 7. After making corrections for sag produced by the weight of glaze, ordinary firing sag, and sag due to strain between glaze and body, it was found that an appreciable amount of sag was attributable to glaze penetration.

It was concluded that (1) some sag was due to glaze penetration, (2) one-fire ware was penetrated more readily than two-fire ware, and (3) the boron glaze penetrated more than did the lead glaze. Although the sag test gave indications of a reaction that had progressed considerably, it yielded little information relative to the beginning of such reactions nor could a number of specimens be studied simultaneously. Because of these results, the rod test was devised.

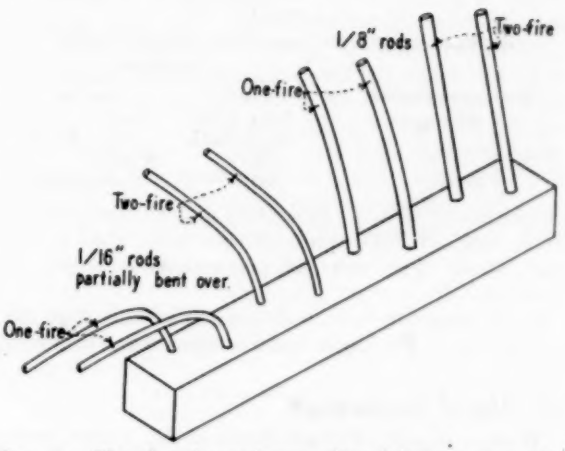

FIG. 1.—Glazed rod specimens after firing to cone 10.

(2) Rod Test

The test body (+2% gum tragacanth) was made up to plastic consistency and extruded through a $\frac{1}{16}$-in. orifice. The extruded specimens were dried hanging vertically and were cut into 4-in. lengths. Some of the rods were then bisqued, and the raw and bisqued rods were given similar treatment. They were glazed by dipping, leaving only $\frac{3}{4}$ in. unglazed at one end. The glazes were maintained at 60°Bé. and were applied to a dry thickness of 0.022 ± 0.003 in. The addition of 1% starch to the glazes prevented the slaking of the raw bodies.

The glazed and unglazed rods were set in a refractory plaque at an angle of 8 degrees from the vertical, much in the manner of cone setting. The unglazed portion of the rods extended $\frac{1}{2}$ in. into the refractory and $\frac{1}{4}$ in. above. The plaque was set in a muffle kiln in proximity to standard cones and fired at the rate of 50° per hour. They were continually observed and the cones at initial and final bend were recorded (Fig. 1).

The cone at which the rod shows the first perceptible movement from its set position is considered to be the cone of initial bend and that at which the rod bends sufficiently to touch the refractory plaque is the cone of final bend. Bending occurs in the form of an arc extending from the tip of the specimen to the lowest point of glaze and body contact. Check runs were made in each test.

The difference (in cones) between the heat-treatment necessary to cause the initial bend of an unglazed rod and that necessary to cause the initial bend of the same rod glazed is called the "cone depression" caused by that glaze and is considered to be a measure of glaze penetration.

Rods of two different diameters, $\frac{1}{8}$ in. and $\frac{1}{16}$ in. in size, were prepared from the semivitreous body used in the sag test. Raw and bisqued rods and raw and bisqued bars were glazed with six different glazes.

TABLE I
RESULTS OF PRELIMINARY SAG AND ROD TESTS

Order of penetration	Specimens	
	One fire	Two fire
1 (greatest)	ZnO, ZrO_2	ZnO
2	MgO, SnO_2	ZrO_2, SnO_2
3	CaF_2	MgO
4 (least)	BaO	CaF_2, BaO

Substitutions of 0.325 equivalent of ZnO, ZrO_2, MgO, SnO_2, CaF, or BaO were made for 0.325 CaO in the base glaze. The order of penetration is shown in Table I.

In all cases, the $^1/_8$-in. rods came down later than the $^1/_{16}$-in. rods. The $^1/_{16}$-in. rod was selected as a standard test rod.

(3) Use of Spectrograph

Wedges of special shape shown in Fig. 2 were made of the semivitreous body (part I, section II (1)). Glazes containing zirconium and tin oxides as substitutes for CaO were applied to a dry thickness of 0.022 in. on side *A* (see Fig. 2). Raw and bisque (cone 9) specimens were glazed, and representative specimens of each combination were fired to cones 5 and 9.

After cooling and measuring the various wedge thicknesses, the ridge of the wedge was knocked off in sections by sharp blows with a mallet. The various identified segments were crushed in a diamond mortar and ground in an agate mortar. The samples were analyzed for all glaze components. Spectrographic analyses had previously been made of the fired glazes and of the raw and bisqued body to check the distribution of glaze and body components.

A large Littrow prism spectrograph with a cupped carbon electrode for holding the sample was used. Equal samples by volume were fired for 30 seconds at 15 amperes. Table II shows a sample data sheet used and Table III gives a summary of the results obtained.

There was a trace of tin in the zirconium glaze which tended to follow the lead as it penetrated the body. Calcium existed in approximately the same amount throughout the body and was present in the raw glaze as well as in the body. Potassium was found in the glaze but not in the body.

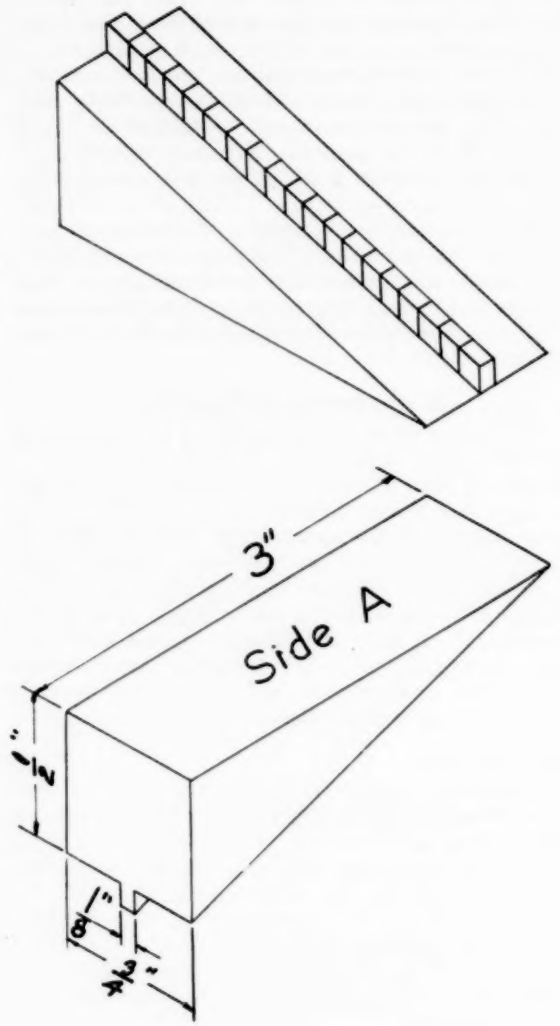

FIG. 2.—Wedge-shaped specimens used for spectrograph test.

II, CORRELATION OF GLAZE-PENETRATION WITH GLAZE-FIT DATA

I. Glaze Penetration Tests

Having developed what was considered to be a satisfactory test for the determination of glaze penetration, the next step was to determine what effect such penetration would have on glaze fit.

(1) Preliminary (with Sag Bars)

A series of bodies was prepared based on the semivitreous body (part I, section II (1)) in which the flint content was varied from 16 to 50% in increments of 2%. Rings for determining the character of the stress and special specimens for noting glaze fit were prepared (Fig. 3). The lead and boron glazes were applied to raw and bisqued (cone 10) specimens and fired to cone $6^1/_2$. The rings were measured and cut in the usual manner, and the other specimens were examined for glaze defects. See Table IV for summary and results of sag tests run previously.

There are definite indications that glaze penetration affects glaze fit.

(2) With Rods

To consider other oxides than lead and boron, it was necessary to determine the effect of the various proposed substitutes on the maturing range of the glaze. The substitution in many instances made the glaze too refractory, and it became necessary to change the base glaze by introducing 0.145 equivalent of PbO for CaO.

TABLE II

SAMPLE DATA SHEET SPECTROGRAPHIC ANALYSIS*

Sample	Amperes	Exposure	Electrode setting
Fe standard	6	10	9
Zirconium glaze c/5	15	30	12
Thin edge of wedge	15	30	15
Middle of wedge	15	30	18
Thick edge of wedge	15	30	21
Fe standard	6	10	24
Zirconium glaze c/9	15	30	27
Thin edge of wedge	15	30	30
About middle of wedge	15	30	33

* Voltage 120, slit 1.6, position 4 throughout.

The following substitutes in the base glaze were selected: ZnO, ZrO_2, SnO_2, MgO, CaF_2, and BaO.

The glazes were applied to $^1/_{16}$-in. rods of the semivitreous body, and the rod test for determining glaze penetration was run. Using the semivitreous body as a base, bodies were prepared in which the flint content was varied from 6 to 64% in increments of 2%. Glaze specimens (Fig. 3), raw and bisqued at cone 9, were sprayed with the different glazes. Representative specimens were fired to cones 6, 9, and 12. The specimens were examined for crazing and shivering three days after removal from the kiln. From information thus obtained, the body containing minimum flint without crazing and the body containing maximum flint without shivering for each glaze were selected for study by the ring test.

The compositions of the various bodies selected are shown in Table VI. Raw and bisqued rings were glazed and fired to cones 9 and 12. The rings were cut in the usual manner and the change in distance between ring marks was determined.

TABLE III

SUMMARY OF DATA OBTAINED WITH SPECTROGRAPH

Applied to	Gloss fire	Thickness of body to penetrate (in.)	Lead	Tin	Zironium
		Zirconium glaze			
Raw body	Cone 5	0.05	Large trace	Same as lead but	Large trace
	"	.33	Small trace	somewhat less	Small trace
	"	.42	" "		" "
	Cone 9	.05	Large trace	Same as lead but	Trace
	"	.18	Trace	somewhat less	"
	"	.34	"		None
Body bisqued at cone 9	Cone 5	.06	Trace	Same as lead but	Trace
	"	.30	"	somewhat less	Small trace
	"	.46	"		" "
	Cone 9	.04	Trace	Same as lead but	Trace
	"	.30	"	somewhat less	"
	"	.43	Small trace		"
		Tin glaze			
Glaze applied to raw body	Cone 5	0.04	Large trace	Large trace	
	"	.24	Small trace	Small trace	
	"	.42	None	None	
	Cone 9	.05	Large trace	Large trace	
	"	.31	Small trace	Small trace	
	"	.42	" "	" "	
Glaze applied to body bisqued at cone 9	Cone 5	.14	Trace	Trace	
	"	.31	"	"	
	"	.39	"	"	
	Cone 9	.04	Trace	Trace	
	"	.29	"	"	
	"	.43	"	"	

The formula of the resulting base glaze and that used throughout the remainder of the study was as follows:

Base glaze

$$\left.\begin{matrix}0.090\ K_2O\\0.140\ Na_2O\\0.300\ CaO\\0.145\ PbO\\0.325\ RO\end{matrix}\right\}\ 0.30\ Al_2O_3\quad 2.8\ SiO_2$$

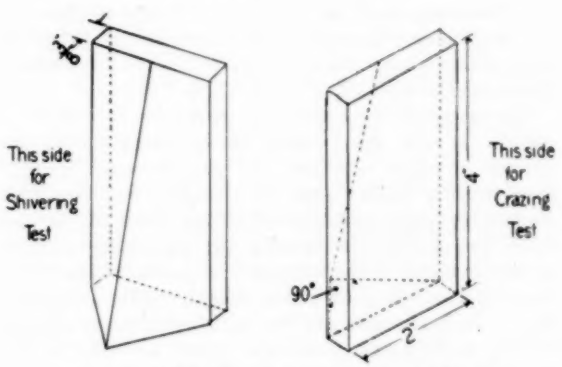

FIG. 3.—Shivering and crazing test specimen.

TABLE IV

SUMMARY OF PRELIMINARY GLAZE-FIT DATA

Glaze	Crazing: When % of flint decreased to (%)	Crazing: When ring corresponding expansion was (mm.)	Shivering: When % of flint increased to (%)	Shivering: When corresponding ring contraction was (mm.)	Sag (in.)
			One fire		
Lead	16	0.22	46	1.0	0.223
Boron	14	0.15	54+	1.58	.386
			Two fire		
Lead	20	0.15	50	.98	.008
Boron	16	0.08	50	1.15	.046

TABLE V

RELATION BETWEEN INITIAL BENDING TEMPERATURE OF GLAZED RODS* AND RANGE IN FLINT CONTENT BETWEEN SHIVERING AND CRAZING

Glaze containing 0.325 equivalent of	Range in flint content between crazing and shivering (%)			Initial bending of rods and "cone depressions" in cones		
	Cone 6	Cone 9	Cone 12	Unglazed rod	Glazed rod	Cone depressions
			One fire			
ZnO	42	48	48	10	3	7
ZrO_2	Immature	44	44	10	3	7
SnO_2	36	40	40	10	5	5
MgO	34	34	34	10	5	5
CaF_2	Immature	34	34	10	6	4
BaO	28	34	34	10	7	3
			Two fire			
ZnO	36	44	44	13½	6	7½
ZrO_2	30	40	40	13½	7	6½
SnO_2	32	38	38	13½	7	6½
CaF_2	26	30	30	13½	8	5½
MgO	32	30	30	13½	8	5½
BaO	24	30	30	13½	8	5½

* Rods 1/16 in.

TABLE VI

COMPOSITION OF BODIES USED IN FINAL RING TESTS AND RESULTS

Glaze	Glaze applied to	Composition (%)						Ring expansion or contraction			
								One fire		Two fire	
		Flint	EPK Fla. kaolin	No-Karb clay	Ky. No. 4 ball clay	C & C ball clay*	Buckingham feldspar	Cone 9	Cone 12	Cone 9	Cone 12
ZnO	Raw bisque	10	16.62	16.62	24.84	13.89	18.00	+0.019	+0.044	+0.030	+0.070
ZrO_2	Raw	12	16.25	16.25	24.31	13.57	17.60	+0.046	+0.014		
SnO_2	"	16	15.51	15.51	23.24	12.94	16.80	+0.007	+0.024		
ZrO_2	Bisque	"	"	"	"	"	"			+0.044	+0.050
SnO_2	"	18	15.14	15.14	22.72	12.61	16.40			+0.007	+0.022
MgO	Raw	26	13.65	13.65	20.56	11.34	14.80	+0.040	+0.031		
BaO	Raw bisque	"	"	"	"	"	"	+0.058	+0.047	+0.070	+0.054
CaF_2	" "	28	13.29	13.29	20.05	10.96	14.40	+0.014	+0.010	+0.018	+0.016
MgO	Bisque	"	"	"	"	"	"			+0.020	+0.006
SnO_2	Raw bisque	52	8.87	8.87	13.24	7.42	9.60	−0 106	−0.097	−0.106	−0.104
ZrO_2	" "	"	"	"	"	"	"	−0.094	−0.150	−0.146	−0.137
ZnO	Bisque	"	"	"	"	"	"			−0.282	−0.218
ZnO	Raw	54	8.51	8.51	12.68	7.11	9.20	−0.208	−0.187		
MgO	Bisque	"	"	"	"	"	"			−0.138	−0.193
CaF_2	"	"	"	"	"	"	"			−0.138	−0.170
BaO	"	"	"	"	"	"	"			−0.146	−0.138
MgO	Raw	56	8.14	8.14	12.13	6.79	8.80	−0.134	−0.173		
BaO	"	"	"	"	"	"	"	−0.194	−0.194		
CaF_2	"	58	7.77	7.77	11.57	6.47	8.40	−0.144	−0.207		

* Champion and Challenger ball clay.

II. Results

The results of the glaze-penetration tests are given in Table V. The cone of initial bending of the glazed rods, the cone of initial bending of the unglazed rods, and the cone difference between the two (cone depression) are given.

The results of the variation in flint content of the body on glaze fit are given in Table V and Fig. 4.

Assuming that there is a uniform change in glaze stress with change in flint content of the body, it is possible to determine the comparative order of change for the various glazes per unit change in the flint content. Considering any glaze-body combination, the distance between the ring marks will show the greatest increase when the tension is greatest (close to the crazing point) and will show the greatest decrease when compression is the greatest (close to the shivering point). By dividing the total change in the distance from that when the opening is greatest (close to the crazing point) to that where the opening is smallest (close to the shivering point) by the percentage change in flint content producing such a change, the change in distance per percentage change in flint content is obtained. Such values have been determined for the various glazes studied and are given in Table VII.

The slopes of the curves are shown in Figs. 5, 6, 7, and 8. It was also possible by interpolation, to determine the flint content that should result in zero glaze stress. These values are also given in Table VII. As for the more penetrating glazes, ZnO, ZrO_2, and SnO_2, the changes in opening per percentage change in flint content of the body are, in general, lower than those of the less penetrating glazes, MgO, CaF_2, and BaO. In both the one-fire and two-fire specimens fired at cones 9 and 12, the ZnO glaze, though the best penetrant, shows a comparatively high change in the

TABLE VII

EFFECT OF FLINT ON STRESS AS SHOWN BY RING TEST

Glaze	Change in opening (mm.)/% change in flint				Flint content producing 0 stress			
	Cone 9		Cone 12		Cone 9		Cone 12	
	One fire	Two fire	One fire	Two fire	One fire	Two fire	One fire	Two fire
ZnO	0.0052	0.0074	0.0053	0.0069	13.5	14.5	19.0	20.0
ZrO_2	.0035	.0053	.0041	.0052	25.2	21.5	15.5	22.5
SnO_2	.0037	.0033	.0034	.0037	17.2	18.0	20.0	19.5
MgO	.0058	.0061	.0068	.0077	33.0	30.0	30.5	28.5
CaF_2	.0084	.0076	.0080	.0069	30.0	32.5	29.5	30.0
BaO	.0053	.0060	.0072	.0071	33.0	36.0	33.0	33.5

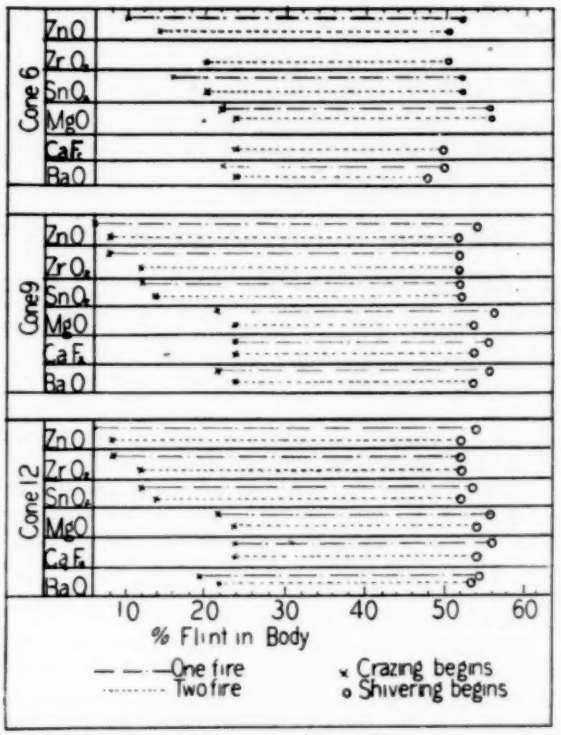

FIG. 4.—Crazing and shivering limits of base glaze +0.325 equivalent of various substitutes.

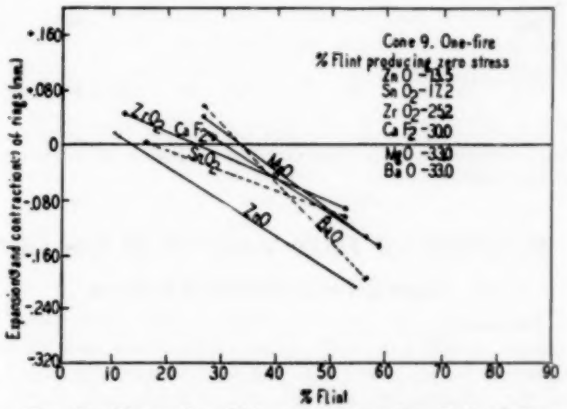

FIG. 5.—Expansion (+) and contraction (−) of rings with different glazes when applied to bodies of varying silica content.

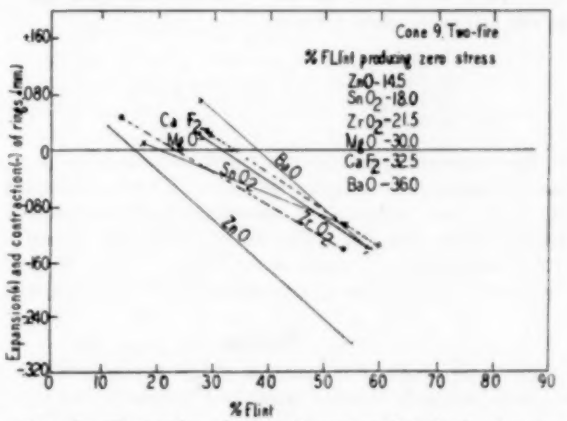

FIG. 6.—Expansion (+) and contraction (−) of rings with different glazes when applied to bodies of varying silica content.

cone 9 specimen. The change, moreover, in opening per percentage change in flint content is greater in all cases with the two-fire than with the one-fire specimens. These comparatively small rates of change in the case of greater penetration are considered to explain the rather long ranges of fit associated with it (Fig. 4). The more penetrating glazes (ZnO, ZrO_2, and SnO_2) are evidently free from stress even on bodies of low flint content.

The linear thermal expansions of the various glazes (calculated by use of Mayer and Havas factors) was (all $\times 10^{-7}$) ZnO 83, ZrO_2 82, SnO_2 81, MgO 79, and BaO 87.

It is evident from these figures that ordinary changes in thermal expansion resulting from the use of various substitutes do not account for the actual results. According to these figures, the MgO glaze should fit (no crazing) a body of lower flint content than would the glazes containing SnO_2, ZrO_2, or ZnO. This, however, was not true. The barium glaze, which requires a body of comparatively high flint content to throw it into compression, shows an extremely short range of fit which the expansion does not explain.

III. Conclusions

Glaze penetration is a factor that influences the glaze fit of a semivitreous body. Glazes that penetrate the body most were found to fit bodies of appreciably greater ranges in flint content than did less penetrating glazes. Their stresses, moreover, were found by the ring test to be less affected by changes in the flint content of the body. The more penetrating glazes were under compression in bodies of comparatively low flint content.

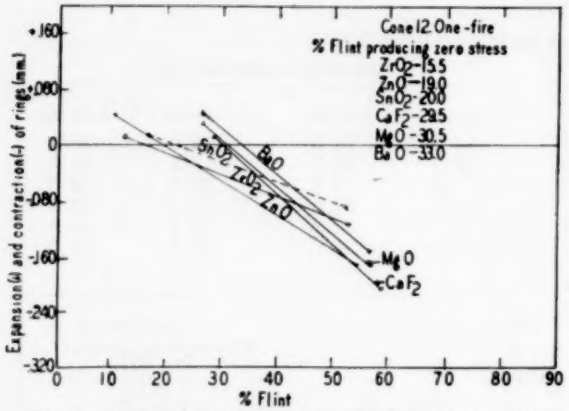

FIG. 7.—Expansion (+) and contraction (−) of rings with different glazes when applied to bodies of varying silica content.

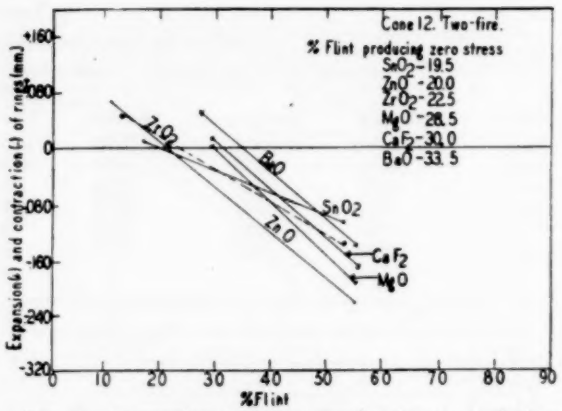

FIG. 8.—Expansion (+) and contraction (−) of rings with different glazes when applied to bodies of varying silica content.

III, EFFECT OF FLUX VARIATION ON GLAZE PENETRATION INTO VARIOUS BODIES

I. Chemical and Mineral Variations

Inasmuch as it was to be expected that glaze penetration would vary with glaze composition and with different bodies, tests were run to determine the effect of the substitution of 0.325 mol. of BaO, B_2O_3, Bi_2O_3, CaF_2, $Ca_3(PO_4)_2$, CdO, Cr_2O_3, CuO, Fe_2O_3, Li_2O, MgO, MnO_2, MoO_2, Na_2UO_4, NiO, PbO, Sb_2O_3, SeO_2, SnO_2 SrO, TiO_2, UO_3, ZnO, and ZrO_2 for 0.325 mol. of CaO, in the following glaze formula:

$$\left.\begin{matrix}0.090\ K_2O\\0.140\ Na_2O\\0.145\ PbO\\0.625\ CaO\end{matrix}\right\}0.30\ Al_2O_3\quad 2.8\ SiO_2$$

The various glazes were applied to rods of each of seven bodies, shown in Table VIII. Check runs were made in every case. The absorptions of the bisqued bodies were wall tile 10%, terra cotta 9%, steatite 12%, cordierite 8%, and hotel china 1.5%; P.C.E. values for the various glazes were determined as usual.

II. Results

By determining the cones of initial bending for the various unglazed bodies (raw and bisqued) and subtracting from these values the cones of initial bending for the corresponding glazed rods, the cone depressions in initial bendings caused by the glazes were obtained. Glazes that penetrate least show slight cone depressions whereas those that penetrate most show the greatest cone depressions. The cone-depression values are given in Table IX as also are the cones of initial bending for the various unglazed bodies (raw and bisqued).

Table X shows the order of decreasing penetration for the various bodies caused by the various substitutions. Those resulting in equal penetration are bracketed; a heavy line is drawn at the average; all above the line penetrated more than average whereas all below penetrated less than average.

The P.C.E. values of the various glazes are given in Table XI as well as the percentages of the various substitutes in the glazes, the melting points of the substitutes, and the average cone depression for all bodies caused by glazes containing the substitutes.

III. Discussion of Results

Penetration as measured by the rod test occurs more readily and more generally in the one-fire rods than in the two-fire rods (Table IX). The average cone depres-

TABLE VIII

BODY COMPOSITIONS

Ingredient	Semi-vitreous (%)	Talc wall tile (%)	Terra cotta (%)	Hotel china (%)	Cordierite (%)	Pyrophyllite wall tile(%)	Steatite (%)
Ky. Old Mine No. 4 ball clay	18.55	12.0	30.0	8.0	77.17	16.0	
Champion & Challenger ball clay	10.00	10.0					
E.P.K. Fla. kaolin	12.13	15.0		6.0		18.0	
Ga. No-Karb kaolin	12.12						
Kamec kaolin				15.5			
Lundy Harris kaolin				10.5			
Perrine stoneware clay			30.0				
Buckingham feldspar	13.20			20.5		3.0	
Flint	34.00			37.5		15.0	
Vanderbilt pyrophyllite		23.0				40.0	
Fire-clay grog			40.0				
Tremoline talc No. 1 (N. Y. State)		40.0			15.67	5.0	100.0
Magnesia					7.16		
Whiting				2.0		2.0	
Magnesite						1.0	

sion for the one-fire rods is, in most cases, greater than that of the two-fire rods and in many cases double. The comparatively high porosity of the one-fire rods during the early part of the heat-treatment is undoubtedly partially responsible for this. Once fired, the pores are fewer and smaller and physical penetration is practically negligible. Certain body components are also free to react with glaze constituents at the interface in the raw body, whereas in the fired body they have reacted with other body components and are not as available for reaction with the glaze.

It is evident that some bodies are penetrated more generally and to a greater extent than others. A comparison between the maximum ($6^1/_4$), minimum (1), an average (2.4) cone depressions of initial bend for the one-fire talc wall-tile body with respective cone depressions for the one-fire steatite body ($11^3/_4$, $6^3/_4$, and $8^1/_2$) shows the differences obtained. This result is readily appreciated when consideration is given to the varying chemical and physical characteristics of glazes and bodies tested (see Table IX). Table IX also shows that glazes penetrate differently on different bodies.

The difference in behavior is particularly marked in the case of the BaO glaze. When placed on the one-fire steatite body, a depression of almost 12 cones occurred and when applied to the one-fire talc wall-tile body there was a depression of only one cone. Numerous other instances can be noted and it is not too surprising when the differences in body compositions are considered.

From the beginning of the fire until the temperature of overfiring is reached, chemical and physical actions, reactions, and changes that affect glaze penetration occur in the body, in the glaze, or involving both. These changes include the decomposition and melting of components, the formation of eutectic melts, changes in viscosity and surface tension of the glaze, changes in the porosity of the body, changes in interfacial tension, chemical reactions between body and glaze components, and volatilization.

Glazes similar to those containing B_2O_3, Bi_2O_3, and PbO, in which the substitutes have very low melting points (Table XI) and whose P.C.E. values are low, evidently have a liquid phase developed at a very low temperature. The liquid may be the melted substitute or a eutectic melt. It contacts the other glaze ingredients and acts as a lubricant permitting the cone to bend at a low temperature. The liquid will also contact the body at the interface and may be absorbed or it may react. In the case of one-fire ware, conditions are favorable for interfacial reactions at comparatively low temperatures. It might be expected, therefore, that such glazes would be generally good penetrants, particularly so with one-fire ware. The data show the B_2O_3 glaze to be an exceptionally good penetrant of all the one-fire bodies except steatite and the PbO glaze an exceptionally good penetrant of all one-fire bodies except the semivitreous and steatite bodies. Both of these glazes were also effective penetrants on two-fire rods.

Although the Bi_2O_3 glaze contains a low-melting substitute (in appreciable quantity) and has a low P.C.E., it did not show the penetrating properties that might have been expected. It was only a fair penetrant and in only one case (pyrophyllite wall-tile body, one-fire) did it show particularly great penetration.

The fact that the glaze containing Sb_2O_3, which oxide melts at 655°C., has the comparatively high P.C.E. value of cone 6 suggests that the melt when formed was too liquid to remain as a lubricant, reacted quickly with the glaze ingredients to form a more refractory mixture, or was absorbed by some of the glaze ingredients. It might be expected, therefore, that early penetration of such a glaze would be poor and probably selective. The data show that there was only one body (cordierite) into which this glaze had greater than average penetration in both one-fire and two-fire rods, and only two one-fire bodies (semivitreous and cordierite) into which penetration was appreciably greater than average.

Glazes containing a substitute such as SeO_2, which sublimes at a low temperature, might be expected to be very selective in penetration if penetrating at all. Three bodies (semivitreous, cordierite, and talc) showed a penetration of greater than average amount and in all cases it was on the one-fire rods.

Glazes containing a substitute such as Cr_2O_3, which is an inert refractory material, would not be expected to show any great amount of penetration except, perhaps, through the preferential reactions of the glaze ingredients with those of the body. The data show the chrome glaze to be a good penetrant only in the case of the semivitreous and pyrophyllite one-fire bodies.

Glazes containing CaO, MgO, SrO, BaO, and Li_2O have comparatively low P.C.E. values (even though the oxides are very refractory in themselves) because low-melting eutectics are formed which permit early cone deformation. The eutectic melt or melts may be formed between the body and glaze as well as between the glaze ingredients only, depending on body composition. In such cases, early and selective penetration might be expected. The data show that these glazes were very selective. The calcium glaze was the poorest, and the magnesium glaze was only slightly better. The barium glaze was particularly good for one-fire cordierite and exceptionally good for one- and two-fire steatite; it was otherwise not notable. The strontium glaze was an exceptionally good penetrant for the one-fire semivitreous body and particularly good in the case of cordierite; otherwise it was mediocre. The lithium glaze was an exceptionally good penetrant for the two-fire steatite body and particularly good in the case of the one-fire pyrophyllite body.

The molybdenum and cadmium glazes proved to be two of the most generally good penetrants; in general, they penetrated the same bodies to approximately the same degree. They were particularly good penetrants of the semivitreous one-fire, cordierite one-fire, and pyrophyllite one-fire bodies.

The zirconium glaze proved to be one of the best penetrants, the explanation for which is not obvious. It showed greater than average penetration into all bodies and in most cases into both one- and two-fire rods. It was the best penetrant for terra cotta (one

TABLE IX

CONE DEPRESSIONS IN INITIAL BENDING OF 1/16-IN. RODS*

	Semivitreous body		Talc wall-tile body		Terra cotta body		Hotel china body		Cordierite body		Pyrophyllite wall-tile body		Steatite body	
	One fire	Two fire	One fire	Two fire	One fire	Two fire	One fire	Two fire	One fire	Two fire	One fire	Two fire	One fire	Two fire
BaO	2	4 1/2	1	1 1/4	1 5/8	2 3/4	6 3/4	4 1/2	10 3/4	1	6	1 1/2	11 3/4	6 1/2
B_2O_3	7	6 1/2	6 1/4	1 1/2	10 1/8	2 3/4	7 3/4	1	11	2 3/4	7 1/2	1 3/4	7 1/4	6
Bi_2O_3	7	4	3	2	5/8	2 3/4	5 3/4	1	6 1/2	4	7 1/2	2 1/4	6 3/4	4
CaF_2	2	3 3/4	1/2	1 3/8	1 5/8	1 3/4	4	3/4	9 1/2	1	4 3/4	1 1/2	10 3/4	2 1/2
CaO	2	3 1/2	1	1 1/4	2 7/8	1	3 3/4	3/4	9 1/2	4	6 1/4	1 1/2	6 3/4	2 1/2
$Ca_3(PO_4)_2$	3 1/2	4 1/2	4	2 1/2	3 5/8	1 3/4	6 3/4	1 1/4	8 1/2	2	5 3/4	2	10 3/4	3 1/2
CdO	9 1/2	5	3 3/4	1 3/4	1 5/8	1 3/4	5 1/4	3	10 3/4	4	8	2 1/2	9 3/4	3 3/4
CoO	7 3/4	3 1/4	1	3/4	5/8	2 1/2	2 1/2	1 1/2	9 3/4	3 1/4	6 3/4	1 1/4	7	3 1/4
Cr_2O_3	7 3/4	4 1/4	2 3/4	1/2	5 1/8	2 1/2	4 3/4	4	6 1/2	2 1/2	7 1/2	2	8 3/4	1 1/2
CuO	7 3/4	4 1/2	4	1 3/8	2 7/8	2 3/4	6	2 1/2	9 3/4	3	6 1/4	1 1/2	7 3/4	3
Fe_2O_3	2	4 1/4	1/2	1 1/2	5 1/8	1 1/2	5 3/	4	3/4	1 3/4	7 1/2	1 1/4	10	3 1/4
Li_2O	2	3 3/4	2	2 1/2	2 7/8	1	5 3/4	4	5 3/4	4	7 1/2	2 1/4	11 1/2	6 1/2
MgO	2	5 1/4	2	1 1/4	7 1/8	1	6 3/4	3/4	9 1/4	2	4	1 1/2	7 1/2	4 1/4
MnO_2	2	3 1/4	2 3/4	1 1/4	5/8	1 1/2	5 3/4	4	9 3/4	3 1/4	7 1/2	1 1/4	10	1 1/4
MoO_2	8 3/4	5	3	1 1/2	3 5/8	1 3/4	7 3/4	3	10 3/4	1 3/4	7	2 1/2	6 3/4	3
Na_2UO_4	2	5	1 1/2	1/2	9 1/8	2 1/2	3 3/4	4	6	1 3/4	6	2	11 1/2	3 3/4
NiO	7 3/4	3 1/4	1 1/4	1 1/2	5/8	1	4 3/4	2 1/2	9 3/4	1 1/4	5	1 3/4	7	3
PbO	3 1/2	5 1/2	4 1/2	1 1/2	6 5/8	4 1/2	9 3/4	3/4	11 1/4	4 1/2	6 3/4	3 1/2	7 1/4	6 1/2
Sb_2O_3	8 1/2	3 1/2	4	1 1/4	1 5/8	1	6	3/4	10 3/4	3	4 3/4	2 1/2	6 3/4	4 1/4
SeO_2	7 3/4	4	1/2	3/8	6/8	1 1/2	2 1/2	1 1/2	10 3/4	1 1/4	7	1 1/2	3 3/4	3 1/4
SnO_2	2	5	2	1	1 5/8	2 3/4	5 3/4	2 1/2	9 1/4	3 1/4	5	2 1/4	10	3
SrO	9 1/2	5	1 1/2	1 1/2	3 5/8	1 3/4	6 1/2	3	10 3/4	1 1/2	7	2	6 3/4	3
TiO_2	8 3/4	5 1/4	3	2	1 5/8	1 3/4	6 3/4	3	4 1/4	4	5 3/4	2	6 3/4	2 3/4
UO_3	2	3 3/4	1	1 1/2	2 7/8	1 3/4	5 3/4	2 1/2	5 3/4	3 1/4	7 1/2	2 1/4	7	4
ZnO	7 3/4	4 1/4	2	2	5/8	3/4	5 3/4	2 1/2	8 1/4	2	7 1/2	1 3/4	6 3/4	4
ZrO_2	8 1/2	5 1/2	4	1	10 7/8	2 3/4	6	5 3/4	10 3/4	4 1/2	8	1 1/2	11 3/4	3 3/4
All glazes Max.	9 1/2	6 1/2	6 1/4	2 1/2	10 7/8	4 1/2	9 3/4	5 3/4	11 1/4	4 1/2	8	3 1/2	11 3/4	6 1/2
All glazes Min.	2	3 1/4	1	3/8	5/8	1	2 1/2	3/4	3 1/4	1	4	1 1/4	6 3/4	1 1/4
All glazes Avg.	5.4	4.4	2.4	1.4	3.4	1.9	5.7	2.5	8.7	2.7	6.1	1.9	8.5	3.9
No glaze (cone of initial bend)	10	13 1/2	9	9 1/2	13 1/8	13	6	8	9	11 1/2	4	12	10	12

* Cone depression = cone of initial bend of unglazed rod minus that of glazed rod.

TABLE X

SUBSTITUTES ARRANGED IN ORDER OF DECREASING PENETRATION OF GLAZES MADE CONTAINING THEM*

Semivitreous body		Talc wall-tile body		Terra cotta body		Hotel china body		Cordierite body	
One fire	Two fire	One fire	Two fire	One fire	Two fire	One fire	Two fire	One fire	Two fire
CdO	B_2O_3	B_2O_3	$Ca_3(PO_4)_2$	ZrO_2	PbO	PbO	ZrO_2	PbO	ZrO_2
SrO	ZrO_2	PbO	Li_2O	B_2O_3	ZrO_2	B_2O_3	BaO	B_2O_3	PbO
TiO_2	PbO	Sb_2O_3	TiO_2	Na_2UO_4	BaO	MoO_2	Cr_2O_3	Sb_2O_3	TiO_2
MoO_2	TiO_2	$Ca_3(PO_4)_2$	ZnO	MgO	SnO_2	TiO_2	Na_2UO_4	MoO_2	CaO
Sb_2O_3	MgO	ZrO_2	Bi_2O_3	PbO	CuO	$Ca_3(PO_4)_2$	Fe_2O_3	ZrO_2	CdO
ZrO_2	Na_2UO_4	CuO	CdO	Cr_2O_3	B_2O_3	MgO	MnO_2	SeO_2	Li_2O
Cr_2O_3	MoO_2	CdO	UO_3	Fe_2O_3	Cr_2O_3	BaO	Li_2O	SrO	Bi_2O_3
NiO	SnO_2	TiO_2	NiO	$Ca_3(PO_4)_2$	Na_2UO_4	SrO	TiO_2	BaO	UO_3
CoO	SrO	MoO_2	MoO_2	MoO_2	CoO	Sb_2O_3	SrO	CdO	SnO_2
SeO_2	CdO	Bi_2O_3	SrO	SrO	TiO_2	ZrO_2	MoO_2	NiO	MnO_2
ZnO	$Ca_3(PO_4)_2$	Cr_2O_3	Fe_2O_3	CaO	UO_2	CuO	CdO	CoO	CoO
CuO	BaO	MoO_2	B_2O_3	UO_2	$Ca_3(PO_4)_2$	UO_3	UO_3	MnO	Sb_2O_3
B_2O_3	CuO	MgO	PbO	Li_2O	CaF_2	SnO_2	NiO	CuO	CuO
Bi_2O_3	Cr_2O_3	SnO_2	CaF_2	CuO	SrO	MnO_2	SnO_2	CaO	B_2O_3
$Ca_3(PO_4)_2$	Fe_2O_3	ZnO	CuO	Sb_2O_3	MoO_2	Fe_2O_3	ZnO	CaF_2	Cr_2O_3
PbO	ZnO	Li_2O	CaO	TiO_2	CdO	ZnO	CuO	MgO	$Ca_3(PO_4)_2$
UO_3	SeO_2	Na_2UO_4	MgO	CaF_2	Fe_2O_3	Li_2O	CoO	SnO_2	MgO
CaO	Bi_2O_3	SrO	MnO_2	SnO_2	MnO_2	Bi_2O_3	SeO_2	$Ca_3(PO_4)_2$	ZnO
Na_2UO_4	UO_3	NiO	BaO	BaO	SeO_2	CdO	$Ca_3(PO_4)_2$	ZnO	Na_2UO_4
MgO	CaF_2	UO_3	Sb_2O_3	CdO	Sb_2O_3	Cr_2O_3	B_2O_3	Cr_2O_3	MoO_2
CaF_2	Li_2O	CaO	ZrO_2	MnO_2	CuO	NiO	Bi_2O_3	Bi_2O_3	Fe_2O_3
MnO_2	Sb_2O_3	CoO	SnO_2	NiO	NiO	CaF_2	MgO	Na_2UO_4	SrO
SnO_2	CaO	BaO	CoO	CoO	MgO	CaO	CaF_2	UO_3	NiO
Fe_2O_3	NiO	CaF_2	Cr_2O_3	SeO_2	Li_2O	Na_2UO_4	Sb_2O_3	Li_2O	SeO_2
BaO	MnO_2	Fe_2O_3	Na_2UO_4	ZnO	Bi_2O_3	CoO	CaO	TiO_2	BaO
Li_2O	CoO	SeO_2	SeO_2	Bi_2O_3	ZnO	SeO_2	PbO	Fe_2O_3	CaF_2

* Vertical braces include all that have equal effect; those underscored with heavy rule indicate average.

TABLE IX (*concluded*)

All bodies one fire			All bodies two fire		
Max.	Min.	Avg.	Max.	Min.	Avg.
11.8	1	5.7	6.5	1.0	3.1
11.0	6.3	8.1	6.5	1.0	3.2
7.5	0.7	5.3	4.0	1.0	2.8
9.5	0.5	4.7	3.8	0.75	1.8
9.5	1.0	4.5	4.0	0.75	2.1
10.8	3.5	6.1	4.5	1.3	2.5
10.8	1.7	7.0	5.0	1.8	3.1
9.8	0.7	5.1	3.3	0.8	2.3
8.8	2.8	6.2	4.3	0.5	2.5
9.8	2.9	6.4	4.5	1.4	2.7
10.0	0.5	4.5	4.3	1.3	2.5
11.5	2.0	5.3	6.5	1.0	3.4
9.3	2.0	5.5	5.3	0.8	2.3
10.0	0.7	5.5	4.0	1.1	2.2
10.8	3.0	6.8	5.0	1.5	2.6
11.5	1.5	5.7	5.0	0.5	2.7
9.8	0.7	5.2	3.3	1.0	2.1
11.3	3.5	7.1	6.5	0.8	3.8
10.8	1.7	6.1	4.3	0.8	2.3
10.8	0.5	4.7	4.0	0.4	1.9
10.0	1.7	5.1	5.0	1.0	2.8
10.8	1.5	6.5	5.0	1.5	2.5
8.8	1.7	5.3	5.3	1.8	2.9
7.5	1.0	4.6	4.0	1.5	2.7
8.3	0.7	5.5	4.3	0.8	2.5
11.8	4.0	8.6	5.8	1.0	3.5

fire), hotel china (two fire), cordierite (two fire), pyrophyllite (one fire), and steatite (one fire). The titanium glaze tended to penetrate the same bodies as did the zirconium glaze but was not as effective.

The zinc and uranium oxide glazes behaved with marked similarity in penetration. In general, they

TABLE X (*concluded*)

Pyrophyllite body		Steatite body	
One fire	Two fire	One fire	Two fire
ZrO_2	PbO	ZrO_2	BaO
CdO	Sb_2O_3	BaO	PbO
Cr_2O_3	MoO_2	Na_2UO_4	Li_2O
UO_3	CdO	Li_2O	B_2O_3
MnO_2	UO_3	CaF_2	MgO
Fe_2O_3	SnO	$Ca_3(PO_4)_2$	Sb_2O_3
ZnO	Li_2O	Fe_2O_3	UO_3
B_2O_3	Bi_2O_3	MnO_2	ZnO
Li_2O	Cr_2O_3	SnO_2	Bi_2O_3
Bi_2O_3	TiO_2	CdO	Na_2UO_4
MoO_2	Na_2UO_4	Cr_2O_3	ZrO_2
SrO	$Ca_3(PO_4)_2$	CuO	CdO
SeO_2	SrO	MgO	$Ca_3(PO_4)_2$
CoO	NiO	PbO	Fe_2O_3
PbO	ZnO	B_2O_3	CoO
CaO	B_2O_3	UO_3	SeO_2
CuO	CaO	NiO	NiO
Na_2UO_4	MgO	CoO	MoO_2
BaO	CaF_2	Sb_2O_3	SnO_2
TiO_2	ZrO_2	TiO_2	SrO
$Ca_3(PO_4)_2$	SeO_2	CaO	CuO
NiO	BaO	MoO_2	TiO_2
SnO_2	CuO	SrO	CaF_2
Sb_2O_3	Fe_2O_3	ZnO	CaO
CaF_2	MnO_2	Bi_2O_3	Cr_2O_3
MgO	CoO	SeO_2	MnO_2

penetrated the same bodies and to the same degree. Only in the case of the pyrophyllite (one fire) body were they particularly effective.

TABLE XI

AMOUNT OF SUBSTITUTE ON PERCENTAGE WEIGHT BASES, MELTING POINTS OF SUBSTITUTES, P.C.E. OF GLAZES, AND AVERAGE CONE DEPRESSIONS

Glaze	Mol. substitute in glaze	Substitute in glaze (%)	Melting point of substitute (°C.)	P.C.E. of glaze	Avg. cone depression (all bodies) One fire	Avg. cone depression (all bodies) Two fire
Bi_2O_3	0.325	36.7	820	08	5.3	2.8
Na_2UO_4	.325	30.3		1	5.7	2.7
$Ca_3(PO_4)_2$	.325	27.8	1700	01	6.1	2.5
PbO	.325	21.7	886	08	7.1	3.8
Sb_2O_3	.325	26.6	655	6	6.1	2.3
UO_3	.325	26.3		3	4.6	2.7
SnO_2	.325	16.1	1625d	02	5.1	2.8
BaO	.325	16.0	1925	04	5.7	3.1
Cr_2O_3	.325	15.9	2435	4¼	6.2	2.5
CdO	.325	13.7	>1426	05	7.0	3.1
MoO_2	.325	13.7	(*)	01	6.8	2.6
ZrO_2	.325	13.3	2690	02½	8.6	3.5
SeO_2	.325	12.1	(†)	02	4.7	1.9
SrO	.325	11.4	2430	02	6.5	2.5
MnO_2	.325	9.7		02	5.5	2.2
ZnO	.325	9.2	1975	04	5.5	2.5
TiO_2	.325	9.1	1825	2½	5.3	2.9
CuO	.325	9.0		08	6.4	2.7
CaF_2	.325	8.8	1378	01	4.7	1.8
NiO	.325	8.6	1990	2½	5.2	2.1
CoO	.325	8.5	935	02	5.1	2.3
Fe_2O_3	.325	8.2	1565	02	4.5	2.5
B_2O_3	.325	8.1	450	08	8.1	3.2
CaO	.325	6.5	2570	3	4.5	2.1
MgO	.325	4.7	2800	01	5.5	2.3
Li_2O	.325	3.6	>1700	08	5.3	3.4

* To MoO_3 which melts at 795°C.
† Sublimes at 315°–317°C.

The behavior of the CaF_2 glaze was similar to that of the CaO glaze. Its greatest penetration occurred with the cordierite body. The $Ca_3(PO_4)_2$ glaze was better than the other lime glazes, showing exceptionally good penetration into the talc wall-tile body (two fire) and much greater than average penetration into the steatite one-fire body.

The iron and manganese glazes behaved similarly, being generally poor penetrants with greatest penetration on the pyrophyllite and steatite one-fire bodies.

The copper glaze was a fairly general penetrant (poor for steatite), showing its greatest penetration on the cordierite and semivitreous one-fire bodies.

The cobalt and tin glazes were among the poorest penetrants. Cobalt showed its greatest penetration into one-fire cordierite and the tin glaze into one-fire steatite.

The nickel glaze was a generally poor penetrant showing greatest penetration in the case of one-fire semivitreous and the one-fire cordierite bodies.

NOTE: Molecular substitution resulted in the substitution of varying amounts of substitutes on a percentage weight basis. To have made substitutions on the latter basis would have involved the selection of a fair and proper percentage, which would have been difficult. The study, involving as it does not only the melting and maturing points of the glaze but also the chemical and physical characteristics of the melt and its activity at the glaze-body interface, makes the choice of a foolproof basis for substitution almost impossible. Before the full import and all the mechanics of glaze penetration will be understood, much work will have to be done. Varying amounts

of substitutes must be studied and there are indications that surprising and useful information will result.

IV. Conclusion

Glaze penetration and the degree to which it occurs will depend on the constituents in the glaze and on the body to which the glaze is applied. It occurs to a greater degree on one-fire bodies than on two-fire bodies. It has been shown that a glaze that is the best penetrant for a particular, one-fire body may not be the best for the same body when bisqued. There is evidently no particular substitute that promotes penetration in all bodies, although the oxides of boron, lead, zirconium, and cadmium proved most generally effective when incorporated in the base glaze under study.

In view of the influence that glaze penetration has on glaze fit, the data presented suggest materials to incorporate in a glaze to improve this property.

Acknowledgment

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USE OF POTASSIUM DICHROMATE METHOD IN DETERMINING IRON CONTENT OF PICKLE ACIDS*

By Edward G. Porst

Abstract

The metallic iron content of sulfuric acid pickle solutions has for many years been determined by the potassium permanganate method. Developments in the field of indicators have made possible the use of potassium dichromate. A description of the method and a discussion of results are given.

I. Introduction

The determination of the equivalent metallic iron content in sulfuric acid pickling solutions is of recognized importance in many enameling plants and especially in those where systematic control of chemical and physical factors is constantly practiced. It is well known that new dilute solutions of sulfuric acid (6%), such as are used in enameling plant pickle tanks, attack sheet steel a great deal faster than old solutions; this condition arises when the iron buildup in old acid solutions becomes excessive. Occasional determinations of the iron content of the pickling acid are therefore required in order to establish when the solution should be discarded. Normally, an iron content of from 5 to 8% is considered the maximum allowable concentration.

In the normal plant control determinations of the iron content of acid, the required accuracy of determination is far less than that of ordinary chemical analysis carried on in the laboratory. Many factors which influence the final accuracy of the results are not even considered, for example, the effect of variations in the specific gravity of the solutions due to the sulfuric acid content and the iron salts content. In such operations, simplicity of methods and equipment, speed of operation, and stability of solutions are important because in most cases the personnel carrying on the operations are not trained chemists and have neither the knowledge nor experience to carry on their operations in the normal analytical chemical laboratory manner. Since merely an approximate knowledge of the iron content is needed, the slight deviations from absolute accuracy are not fundamentally important.

The iron content of sulfuric acid pickle solutions is usually determined by titrating a measured sample of the acid with potassium permanganate; the reaction depends simply on the oxidation by the permanganate of the ferrous iron to ferric iron so that by knowing the iron equivalent of the standardized permanganate solution and its titrated volume, the iron content may be readily calculated.

The use of potassium permanganate has certain disadvantages. Because it is customary to use 0.895 normal solutions, the stability of the solution is not too great and, therefore, care must be used in preventing exposure to light and other conditions which will tend to accelerate the breakdown of the solution. Potassium permanganate solutions, moreover, are not too readily prepared and standardized. The permanganate solutions cannot be used in determining the iron content of muriatic acid solutions without radical changes of method and, finally, permanganate has a bad tendency to stain equipment and personnel.

The use of potassium dichromate as a standard oxidizing solution of ferrous salt solutions has been known for many years although it has never been used as widely as potassium permanganate. One explanation for the greater popularity of permanganate lies, perhaps, in the fact that by virtue of its strong color no indicators are needed for detection of the end point. The use of diphenylamine as an internal indicator, when titrating with $K_2Cr_2O_7$ standard solutions, was recom-

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mended by Knop[1] in 1924; up to that time, detection of the end point was tedious and uncertain since external indicators such as potassium ferricyanide were used.

While it is true that the reduction of dichromate gives the chromic iron a green color (which may confuse the color of the internal indicator if dilute solutions of potassium dichromate are used where very high iron contents are encountered), when a stronger solution, as, for example, a normal potassium dichromate solution is used, the color developed in the determination of iron contents in the range required for pickle-room control, is not such as to confuse the color of the indicator.

One excellent characteristic of the $K_2Cr_2O_7$ standard solution is its stability. For example, Carey[2] stated that a 0.1 *N* solution of $K_2Cr_2O_7$ did not change appreciably in titre during twenty-four years. Another advantage is the fact that dichromate solution in the cold reacts much less readily with organic matter than permanganate[3]; thus the presence of organic inhibitors or other organic matter in pickling acids will not interfere. In addition, $K_2Cr_2O_7$ standard solutions are more easily prepared than $KMnO_4$ solutions since the presence of traces of organic matter in the distilled water are not objectionable. In 1938, Stufft[4] recommended the use of potassium dichromate for pickle-room control purposes, but there is no information available indicating that the method was used commercially. During the course of some work on a project unrelated to enameling operations, the necessity of making a considerable number of iron determinations arose. Experiments were conducted comparing the use of potassium permanganate and potassium dichromate with the result that the use of $KMnO_4$ was discarded and $K_2Cr_2O_7$ substituted. In view of these facts relating to $K_2Cr_2O_7$ solution, it was decided to test it against the $KMnO_4$ method on actual samples of pickling acid obtained from various enameling plants.

II. Method of Procedure

For purposes of analysis, seven samples of sulfuric acid-pickling solution were used. The specific gravity of each solution was determined by means of a hydrometer.

A standard solution of $KMnO_4$ was prepared[5] by dissolving 28.8 gm. of the salt in sufficient boiling distilled water to make one liter solution and filtering through an asbestos mat after 24 hours. To standardize this solution, 2 gm. of pure sodium oxalate were transferred to a beaker, together with 200 ml. of distilled water and 50 to 60 ml. c.p. concentrated H_2SO_4 (sp. gr., 1.84). The solution was heated to 80°C., and after complete solution of salt, it was titrated dropwise with the $KMnO_4$ solution until the first permanent appearance of pink color. The normality of $KMnO_4$ solution was calculated by formula (1).

$$\text{Normality} = \frac{2 \text{ gm. } Na_2C_2O_4}{\text{Ml. } KMnO_4 \times 0.0670} \qquad (1)$$

If desired, the sodium oxalate method of the Bureau of Standards as set forth under Provisional Certificate of Analysis for Sample 40 d, may be used.

A standard solution of potassium dichromate was prepared[6] by dissolving 44.1 gm. of the salt in distilled water, filtering, and making up to one liter. For standardization of the solution, the following reagents were required: (1) 25% sulfuric acid (25% c.p. H_2SO_4 of sp. gr. 1.84 plus 75% distilled H_2O by volume); (2) phosphoric-sulfuric acid solution (1/3 c.p. H_2SO_4 sp. gr. 1.84 and 2/3 c.p. phosphoric acid 1.71 sp. gr. both by volume); (3) diphenylamine indicator (dissolve 1 gm. diphenylamine salt in 100 ml. c.p. H_2SO_4 sp. gr. 1.84) (or, 100 ml. 60% acetic acid); and (4) c. p. ferrous ammonium sulfate.

In a 400-ml. beaker were placed 7.000 gm. of ferrous ammonium sulfate ($FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$), 75 ml. of distilled water, and 10 ml. of 25% sulfuric acid mixture. When the solution of the salt was complete, 15 ml. of phosphoric-sulfuric mixture and three drops of diphenylamine indicator were added, and the mixture was titrated with the dichromate solution until a deep purple color persisted. The normality of the solution was calculated by formula (2).

$$\text{Normality} = \frac{7.000 \text{ Fe}(NH_4)_2(SO_4)_2 \cdot 6H_2O \times \% \text{ purity} \times 100}{\text{Ml. } K_2Cr_2O_7 \text{ sol. tit.} \times 0.3922} \qquad (2)$$

The iron content of pickling acid was determined by the permanganate method as follows*:

Ten milliliters of the sample were transferred to a 400-ml. beaker, 160 ml. of distilled water and 40 ml. of 25% H_2SO_4 solution were added, and the standard permanganate was added dropwise until a permanent pink color persisted. The "apparent" iron content was calculated from formula (3).

$$\text{Ml. } KMnO_4 \times \text{normality} \times \frac{0.05584}{10} \times 100 = \% \text{ Fe} \qquad (3)$$

The "true" iron content was obtained by dividing the percentage of "apparent" iron by the specific gravity of the pickle solution.

The analysis of iron content in pickling acid was determined by the dichromate method as follows:

Ten milliliters of the pickle solution were transferred to a 400-ml. beaker and 75 ml. of distilled water, 15 ml. of phosphoric-sulfuric acid mixture, and three drops of diphenylamine indicator were added. The solution was titrated with the $K_2Cr_2O_7$ standard solution until a deep permanent purple color was obtained.

[1] J. Knop, "Diphenylamine as Indicator in Titration of Iron with Dichromate Solutions," *Jour. Amer. Chem. Soc.*, **46**, 263 (1924).

[2] W. M. Carey, "Stability of Tenth Normal Potassium Dichromate Volumetric Solution," *Jour. Amer. Pharm. Assn.*, **16**, 115 (1927).

[3] L. A. Sarver, "Determination of Ferrous Iron Silicates," *Jour. Amer. Chem. Soc.*, **49**, 1473 (1927).

[4] P. C. Stufft, "Control in Pickling Room," *Amer. Enameler*, **11** [1] 17–18, 26 (1938); Enamel Bibliography, 1944 ed., p. 268.

[5] W. F. Hillebrand and G. E. F. Lundell, Applied Inorganic Analysis, p. 144. John Wiley & Sons, Inc., New York, 1929; *Ceram. Abs.*, **9** [1] 68; [10] 888 (1930).

[6] F. P. Treadwell and W. T. Hall, Analytical Chemistry, Vol. II, p. 578. John Wiley & Sons, Inc., New York, 1942.

* See p. 304 of footnote reference 5.

TABLE I

CHEMICAL ANALYSIS OF IRON IN SULFURIC ACID PICKLING SOLUTIONS

Sample	Sp. gr.	Test No.	$K_2Cr_2O_7$ (ml.) tit.	$KMnO_4$ (ml.) tit.	% Fe "apparent" $K_2Cr_2O_7$ tit.	% Fe "apparent" $KMnO_4$ tit.	% Fe "true" $K_2Cr_2O_7$ tit.	% Fe "true" $KMnO_4$ tit.
A	1.141	1	8.90	9.70	4.90	4.91	4.29	4.30
		2	8.90	9.68	4.90	4.90	4.29	4.29
B	1.100	3	4.62	5.05	2.54	2.56	2.31	2.33
		4	4.65	5.02	2.56	2.54	2.33	2.31
C	1.042	5	0.39	0.40	0.21	0.20	0.20	0.19
		6	0.36	0.41	0.20	0.21	0.19	0.20
D	1.095	7	4.60	4.97	2.53	2.52	2.31	2.30
		8	4.60	4.98	2.53	2.52	2.31	2.30
E	1.099	9	5.78	6.30	3.18	3.19	2.89	2.90
		10	5.81	6.28	3.20	3.18	2.91	2.89
F	1.096	11	6.60	7.17	3.63	3.63	3.31	3.31
		12	6.60	7.17	3.63	3.63	3.31	3.31
G	1.038	13	0.90	1.00	0.50	0.51	0.48	0.49
		14	0.90	1.00	0.50	0.51	0.48	0.49

The "apparent" iron content was calculated from formula (4).

$$\frac{\text{Ml. } K_2Cr_2O_7 \times \text{normality} \times 0.05584 \times 100}{10} = \% \text{ Fe} \quad (4)$$

The "true" iron content was obtained by dividing the percentage of "apparent" iron by the specific gravity of the pickle solution.

The percentage purity of the c.p. ferrous ammonium sulfate was determined[6] by transferring 7.000 gm. of the salt to a 400-ml. beaker, adding 160 ml. distilled water and 40 ml. of 25% H_2SO_4 solution, and titrating the mixture with the standard $KMnO_4$ solution. The percentage purity was then calculated from formula (5).

$$\frac{\text{Ml. KMnO} \times \text{normality} \times 0.3922 \times 100}{7.000 \text{ Fe}(NH_4)_2(SO_4)_2 \cdot 6H_2O} = \% \text{ purity} \quad (5)$$

III. Results and Discussion

The following percentage results were obtained (from two determinations each):

Calculated normality of $KMnO_4$	0.9069
Calculated normality of $K_2Cr_2O_7$	0.9853
Purity of ferrous ammonium sulfate	99.76

(1) There is close agreement between values for metallic iron in sulfuric acid pickling solutions obtained by (*a*) the $KMnO_4$ and (*b*) the $K_2Cr_2O_7$ methods.

(2) The difference between "true" and "apparent" iron content is shown to be as great as 0.60%. It is doubtful whether such variations would become significant in pickle-room practice unless the specific gravity of the pickle solution was much more than 1.141.

(3) Ferrous ammonium sulfate (c.p.) is a good secondary salt for standardizing potassium dichromate solutions. For high accuracy, the purity of the salt should be checked against a standard solution of $KMnO_4$. For ordinary pickle-room control, this precaution is unnecessary; assuming a 100% purity instead of the 99.76% of ferrous ammonium sulfate used in this investigation, calculations show that for iron content of around 5% the error would be approximately plus 0.01% of iron. The sample of ferrous ammonium sulfate used in this work has been in the laboratory for more than one year, which shows good stability during storage. Owing to poor processing by some suppliers, ferrous ammonium sulfate does not have the characteristics of the material noted above. If the material is consistently free from lumps and discoloration, that is, if it has a distinct pale blue-green color, free from brown stains, it is a satisfactory.

(4) The potassium dichromate method is preferable to the potassium permanganate method for the following reasons: (*a*) The former is more stable, especially when used under adverse conditions; (*b*) potassium dichromate is not messy to use; it does not stain the burette as does permanganate (the latter leaves objectionable brown stains on contact with objects); (*c*) potassium dichromate solutions are easier to standardize; no heating is required for solution of the salt and a large sample of the standard salt (ferrous ammonium sulfate) may be used owing to its high molecular weight and low iron content; (*d*) the dichromate method for iron may also be used for testing hydrochloric acid pickle solutions[7] without making radical changes in the prescribed method; and (*e*) in view of Sarver's[3] contention, the dichromate method for iron would be more accurate for testing pickle solutions containing organic inhibitors.

IV. Conclusions

The potassium dichromate method for iron in pickle solutions is superior to the potassium permanganate method because the solution is easier to prepare and standardize, it has greater stability during storage, it may be used for iron in muriatic acid pickle control without radical changes in the method, and it does not stain equipment such as burettes as does permanganate.

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PEMCO CORPORATION
BALTIMORE 24, MARYLAND

[7] W. W. Scott Standard Methods of Chemical Analysis, 5th Ed., Vol. I, p. 471. D. Van Nostrand Co., Inc., New York, 1939.

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